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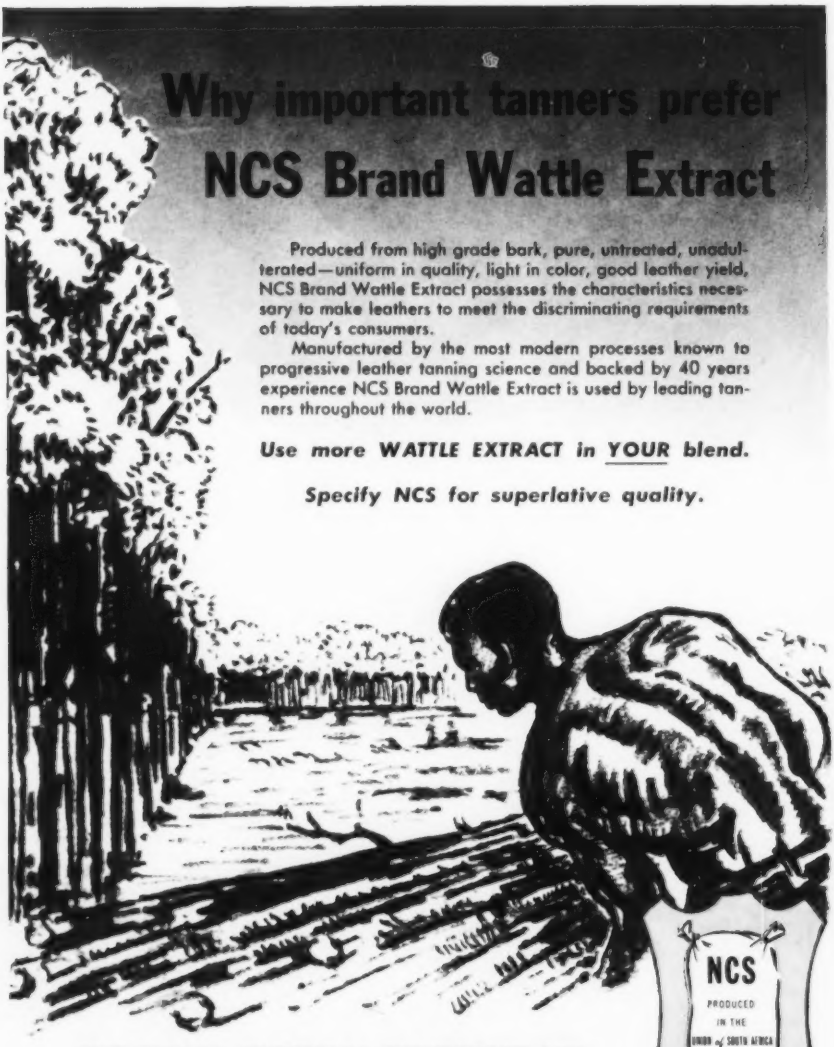

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The Journal

of the

AMERICAN LEATHER CHEMISTS ASSOCIATION

Vol. LV FEBRUARY 1960 No. 2

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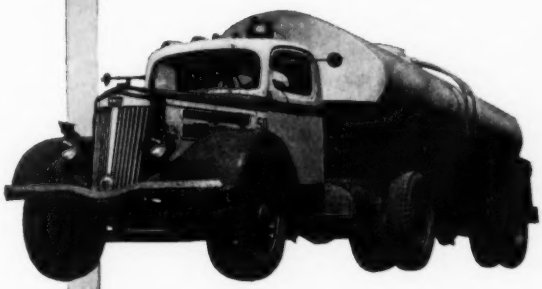

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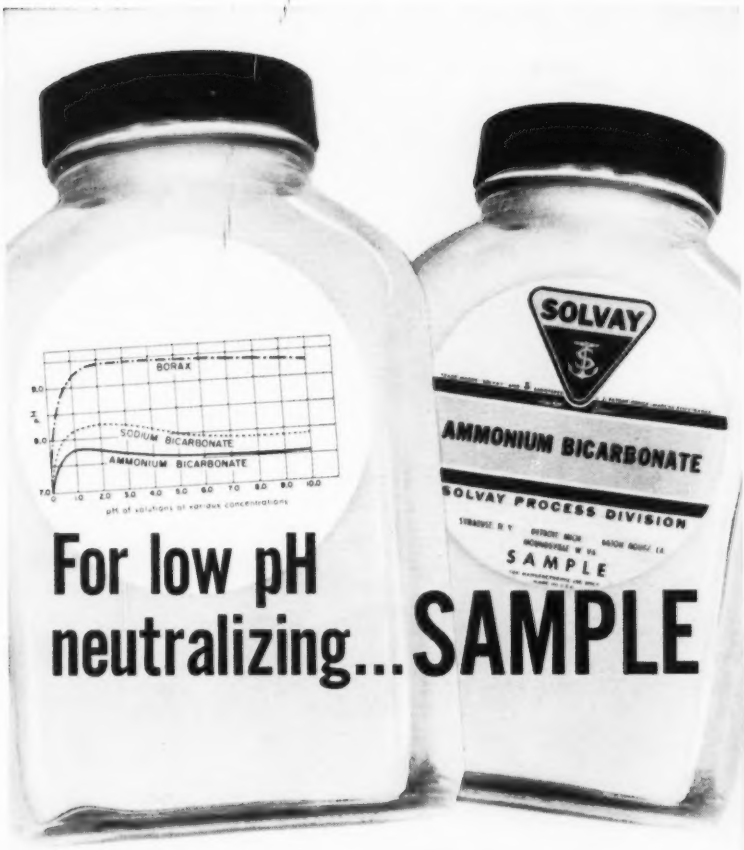

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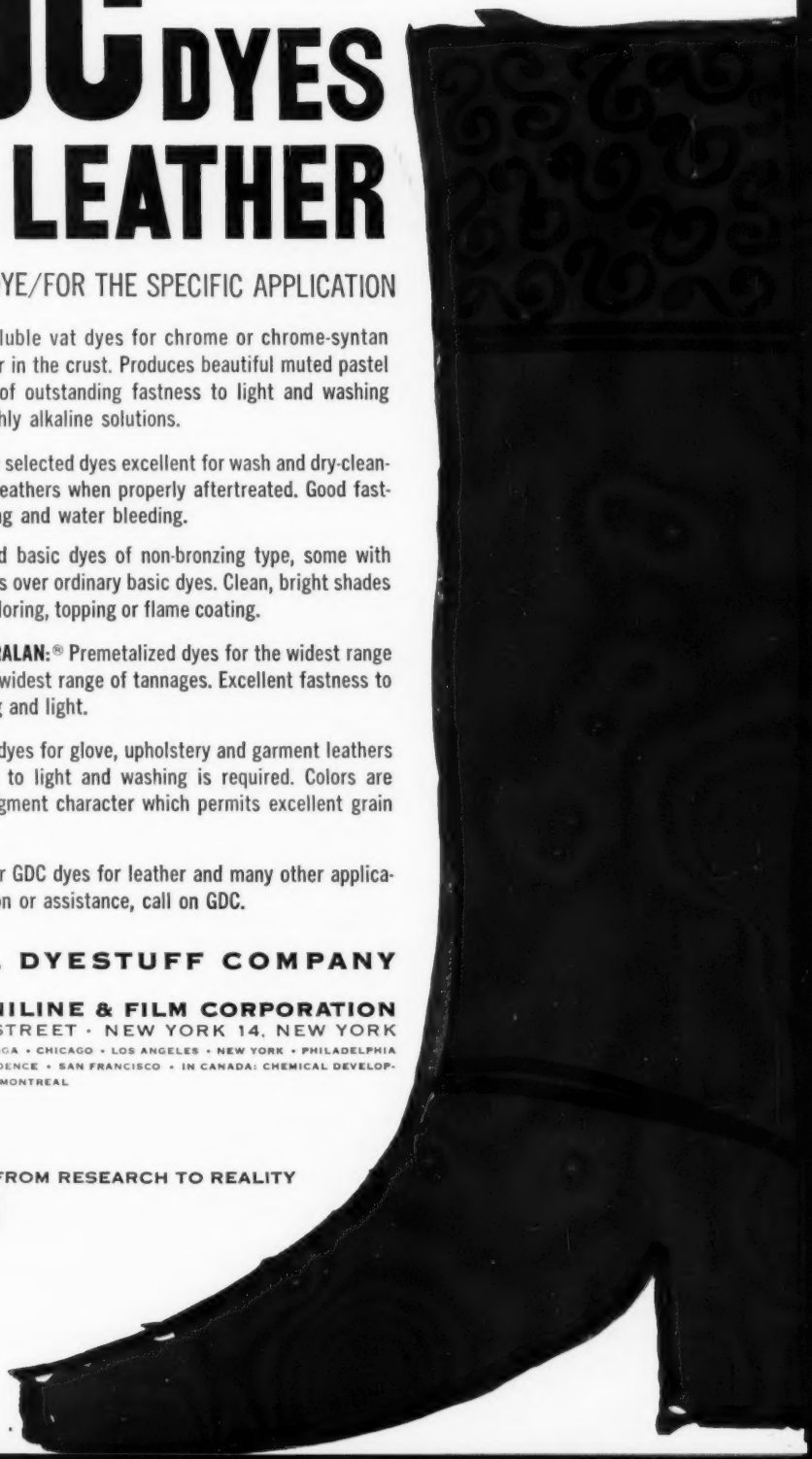

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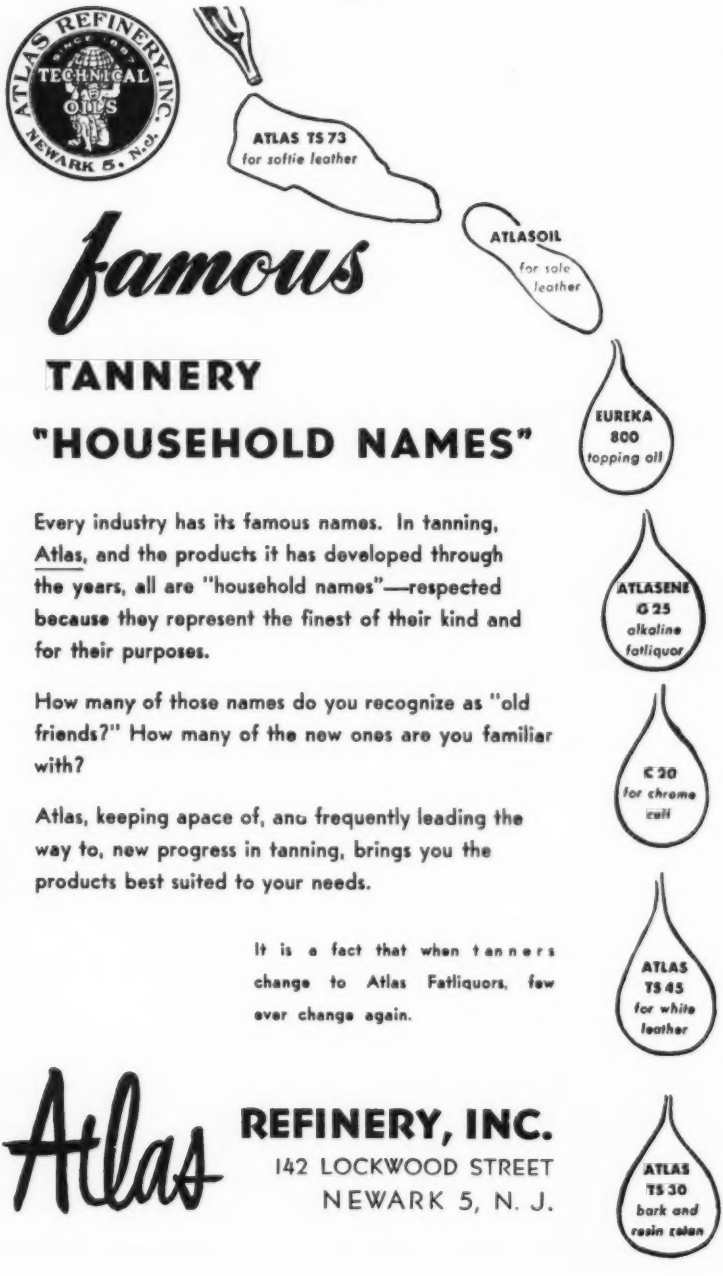

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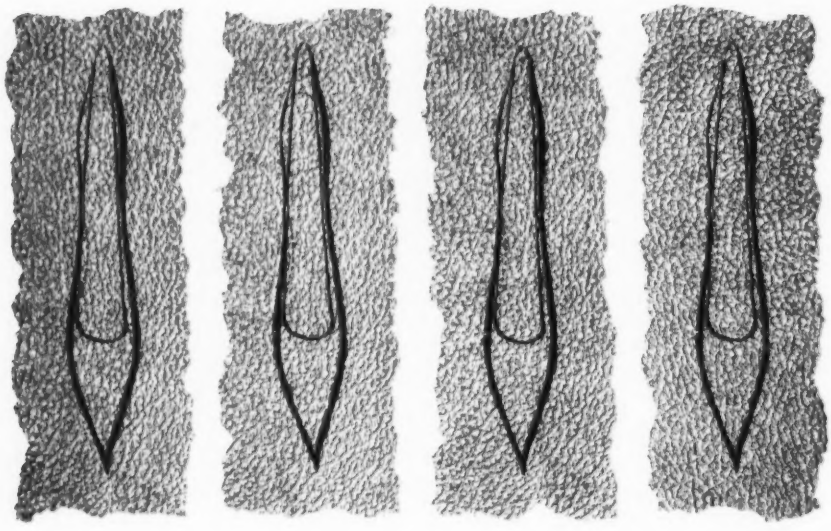

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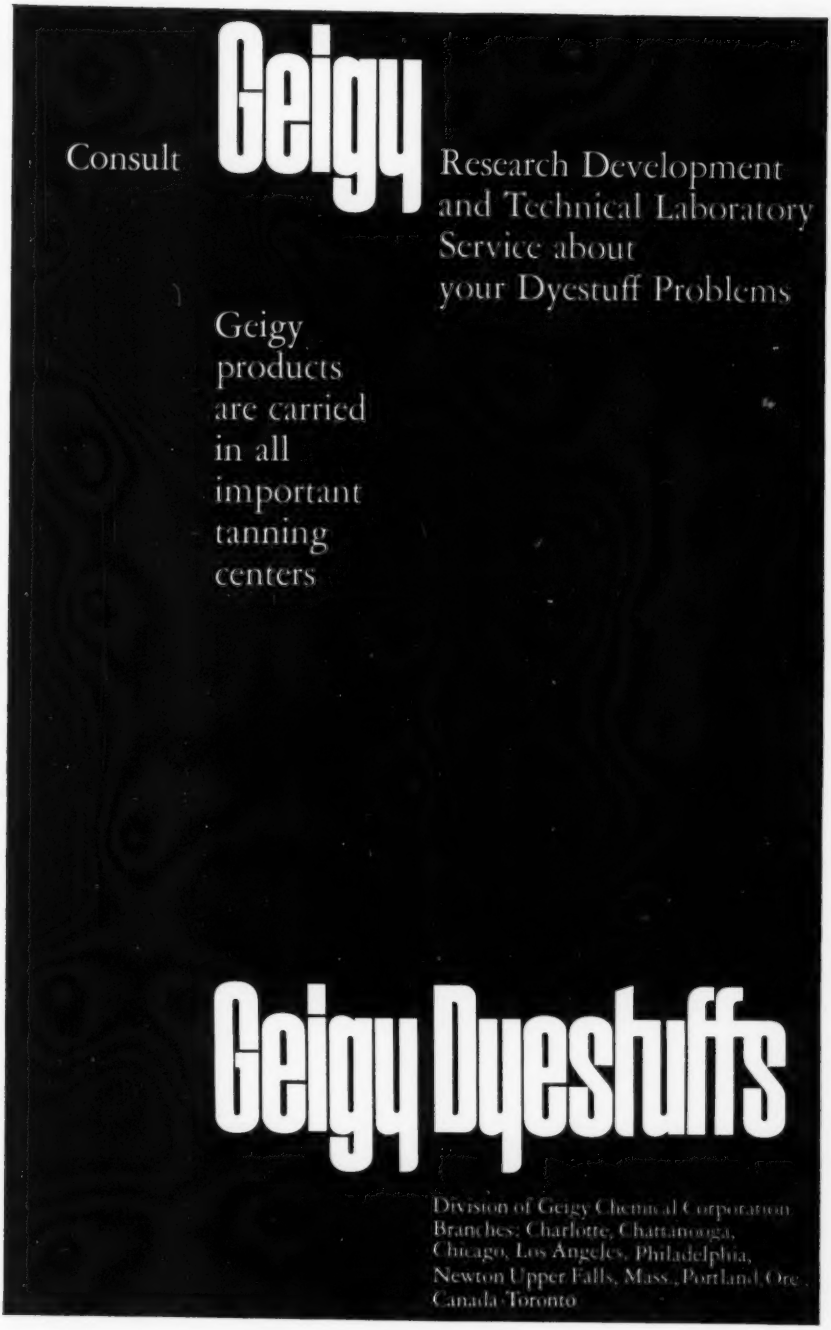
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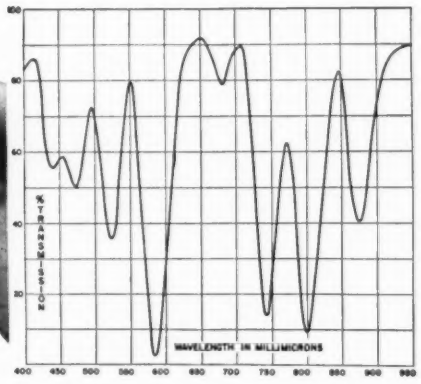

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THE MECHANISM OF SALT STIPPEN FORMATION AND SUGGESTED METHODS OF CONTROL*

J. J. Tancous and F. O'Flaherty

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Tanners' Council Research Laboratory
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Cincinnati 21, Ohio

ABSTRACT

Some aspects of the grain defect known as salt stippen have been investigated. Histological studies have revealed that stippen results in the rupturing of the grain tissues of the hide, that it develops initially during the curing process, and that bacteria are secondarily involved. Spectrographic and chemical analyses have revealed that salt stippen begins as magnesium ammonium phosphate; that after liming, it becomes a double salt adding calcium carbonate to its structure; and that after pickling and chrome tanning, it exists as calcium sulfate. Suggested methods of control include avoiding magnesium in curing salt, avoiding the breakdown of hide tissues before and during cure, and preventing the dehydration of hides in storage.

—×—×—

INTRODUCTION

Eitner (1) in 1913 reported a condition found on the grain of leather to which he gave the name salt stippen (salt specks). Vourloud (2) in 1925, as well as Eitner (1), ascribed the specks to the crystallization of the curing salt or its impurities and claimed that the crystals increase in size during a long storage time. Stather (3) in 1928 reported that the condition occurs on both raw stock and on leather, describing it as small crystal-like protuberances or specks about the size of a pinhead or as craterlike depressions, mottled, and often of irregular star shape. The cause of stippen, according to Rigot (4) in 1932, is the deposit of calcium carbonate within the grain layer. Bergmann, Stather, Hausam, and Liebscher (5), in 1931, called this defect mold sprout because they thought the elevations were caused by a parasitic hair mold which may grow on the hide during storage. This theory continued to create interest as is evidenced by later references (6, 7, 8).

*Presented at the Fifty-fifth Annual Meeting of ALCA, Grand Hotel, Mackinac Island, Michigan, June 16, 1959.

During the period 1955 to 1958 this condition has been observed in hides and leather in the United States and has prompted the present investigation. The salt stippen defects which were encountered consisted of small, irregular starlike elevations on the grain of hide and leather.

APPEARANCE OF STIPPEN

Salt stippen can be observed on the skin or hide after unhairing at the tannery if the stock is carefully examined for the damage. The water-insoluble crystals of stippen on unhaired steerhide are shown in Fig. 1. The cutting on the right shows an irregular star-shaped pattern which is the stippen in large size, while the cutting on the left shows the stippen as smaller structures with less definite patterns.

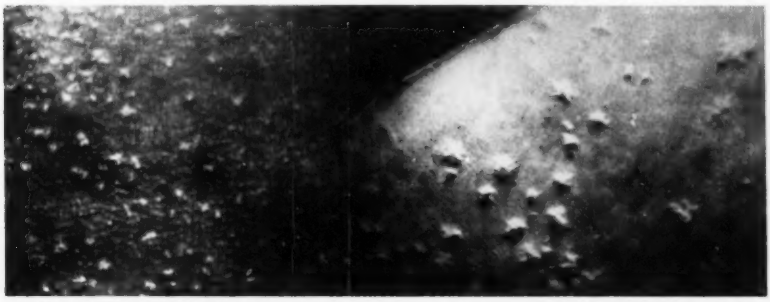

FIGURE 1.—Water-insoluble crystal formations in two cuttings of unhaired steerhide. × 1½.

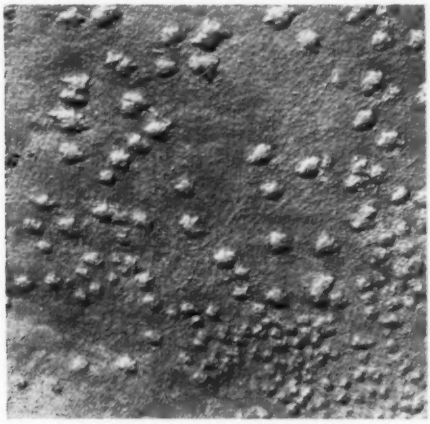

FIGURE 2.—Chrome-tanned side upper leather "in the blue" showing water-insoluble crystal formations. × 1½.

It is possible to have crystallization of soluble salts, such as sodium chloride or magnesium sulfate, which may appear like stippen, but crystal formations from these salts disappear during process because they are soluble. The true salt stippen crystals are water-insoluble and remain in the skin through chrome tanning and appear as illustrated in Fig. 2. The crystals may vary in size as shown in the photograph.

In those shoe upper leathers where the grain has been corrected, the crystal formations may be mechanically removed with the grain. While the crystals may be removed during this operation, indentations remain on the corrected surface where the grain tissues have been ruptured by the stippen formation. The appearance of leather showing the permanent damage caused by stippen on corrected side upper leather is given in Fig. 3.

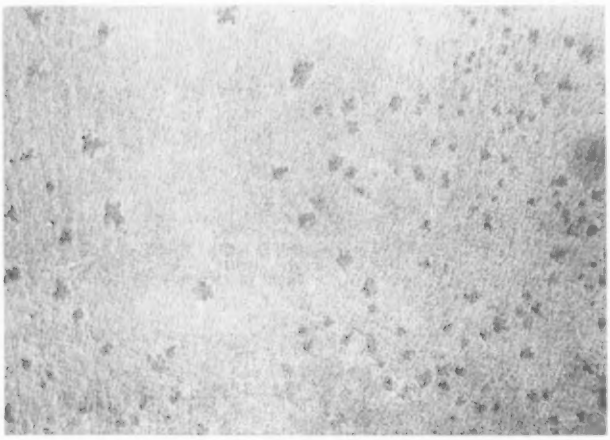

FIGURE 3.—Corrected grain shoe upper leather showing the permanent damage remaining after stippen crystal formations have been removed. $\times 1\frac{1}{2}$.

STRUCTURE OF STIPPEN

To obtain an approximation of the composition of the salt stippen, a quantity of stippen crystals were collected for analysis by removing the specks with a sharp instrument from chrome "in the blue" stock and from finished chrome-tanned leather. The crystals were ashed at 500° C., and the ash was examined on the spectrograph to obtain a preliminary qualitative analysis. This analysis showed that the crystals contained a fair amount of calcium, indicating that the condition occurred on the stock during or before liming.

To check further for the source of the salt stippen formation, cuttings from green-salted hides were obtained from several cooperating tanners who were encountering stippen in various lots of hides. By unhairing one-half of each of these cuttings, it was possible to establish which pieces contained stippen damage. Since the finding of stippen in cured stock is a matter of chance, it was fortunate that about a third of these cuttings showed stippen. Because the other half of the pieces which showed stippen in the limed condition could trace the condition back to the curing operation, they were shaved and examined. Thus, stippen formations were located in cured stock. A cross-sectional view of a typical crystal formation in cured stock is illustrated in Fig. 4.

FIGURE 4.—A photomicrograph made by dark-field microscopy. A cross-sectional view of a mass of crystal formations (salt stippen) in green-salted steerhide. This is a small area in the grain; the section also shows hair follicle fragments. × 80.

To see if bacteria were concerned with stippen formation, many of the defects found in the shaved samples were removed, fixed, sectioned, stained for bacteria, and examined microscopically. Although the cross sections revealed innumerable bacteria on the flesh side and on the surface of the epidermis, they showed no bacteria in the interior of the hide or in the area of the tissues ruptured by the stippen formation. Bacteria invaded the ruptured area only when the tissues of the epidermis had been broken by the crystal formation or by other means. Since it could not be established that bacteria were present in all the stippen areas examined, it is assumed that bacteria are secondary to the condition and not the primary cause.

Masses of stippen were then collected from salt-cured stock unhaired by sweating, and from limed stock. These isolated, impure stippen masses were incinerated at 500° C. until all organic matter had been removed, cooled, and then washed on a 100-mesh screen with distilled water until the crystal masses were free from soluble salts and other impurities. A 45 × magnifying lens was used to examine the crystals for cleanliness. Some of the stippen crystals taken from limed stock are illustrated in Fig. 5. While working with these samples, it was very noticeable that the crystals in the limed stock were larger and easier to collect than those in the sweated samples.

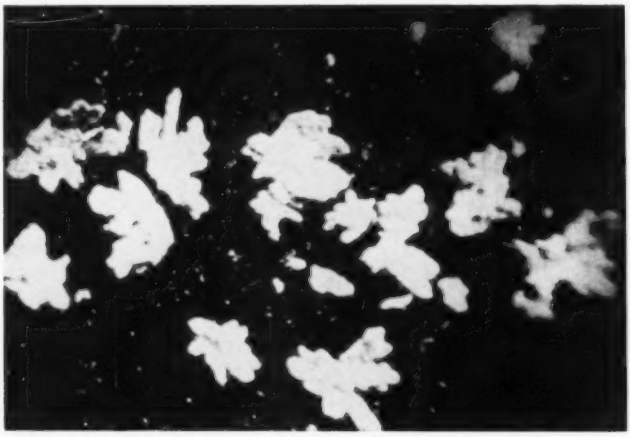

FIGURE 5.—Stippen crystals taken from limed hide. ×15.

Through the cooperation of the Department of Engineering Chemistry of the University of Cincinnati (9), spectrographic analyses of various cleansed stippen samples were made. As mentioned above, stippen obtained from chrome-tanned stock "in the blue" was examined first, and the analyses revealed the presence of calcium as the main constituent. Analyses of crystals of stippen obtained from cured hides and from limed unhaired hides revealed in both instances the presence of calcium, magnesium, and phosphorus.

With the spectrographic analyses as a guide, quantitative analyses were then made. These included colorimetric, gravimetric, and titrimetric methods (10–13). A summary of these analyses is given in Table I. The percentage value of each element is given, and the symbol weight has been calculated by dividing the percentage value of the element by its atomic weight. When the symbol weight or atomic weight of the element represented in the compound is known, the chemical formula can be determined.

TABLE I

RESULTS OF THE QUANTITATIVE ANALYSES ON VARIOUS STIPPEN SAMPLES

Element	Percentage	Symbol Weight	Chemical Formula
Salt-cured Hide Stippen			
P	19.7	0.64	$Mg_2P_2O_7$
Mg	16.5	0.68	
Ca	3.3	0.08	
Limed Hide Stippen			
P	9.7	0.31	$Mg_2P_2O_7 \cdot 4\ CaCO_3$
Mg	7.8	0.32	
Ca	26.4	0.66	
Chrome-tanned Leather Stippen			
P	0.9	0.03	$CaSO_4$
Mg	0.5	0.02	
Ca	21.6	0.54	

It can be noticed that calcium plays a minor part in the salt-cured hide stippen, representing only 3.3% of the total weight, and therefore does not contribute to the formula. The stippen in the cured stock is a type of magnesium phosphate. Since the ratio of magnesium atoms to phosphorus atoms is in the proportion of one to one, the chemical formula most likely is magnesium pyrophosphate, $Mg_2P_2O_7$, derived from magnesium acid phosphate, $MgHPO_4$, or from magnesium ammonium phosphate, $MgNH_4PO_4$.

To establish that magnesium hydrogen phosphate and magnesium ammonium phosphate burn to the pyrophosphate at 500° C., these compounds were each tested for weight loss at various temperatures of incineration. At 500° C. the main loss in weight occurred and agreed with the calculated loss that should occur if the salts were to burn to the pyrophosphate. Since very little additional weight loss occurred at temperatures 600° C. to 1000° C., further evidence that these materials burn to the pyrophosphate at 500° C. was obtained.

To establish the nature of the salt present in stippen taken from cured stock, unashed stippen crystals were tested for ammonia with Nessler's reagent (14). Since a positive test was obtained, it was assumed that the stippen exists as the magnesium ammonium phosphate rather than the magnesium hydrogen phosphate.

In the stippen obtained from limed stock, the calcium represents 26.4% of the total weight as shown in Table I. The calcium contributes to the symbol weight and to the structural formula. A considerable amount of calcium is introduced in the liming operation and contributes to the formation of a double salt.

It was noted above in the stippen from cured stock that there was a ratio of one atom of magnesium to one of phosphorus. After liming there is still a ratio of one magnesium atom to one of phosphorus, but now calcium is also present in a large percentage. In the purified ash from limed hide the stippen is magnesium pyrophosphate which has taken on four calcium atoms. This increase in structure explains why the stippen becomes more accentuated after liming than it was in the salt-cured hide.

During liming there is always a certain amount of calcium carbonate that precipitates, and this was considered as a possible form in which the calcium could attach itself to the magnesium ammonium phosphate to produce the double salt. In two tests made on stippen from limed stock the calcium carbonate suggestion was substantiated. The fact that limed hide stippen effervesced when placed in nitric or hydrochloric acid was an important clue. An additional factor was the fact that calcium carbonate does not burn to the oxide at 500° C. When calcium carbonate was tested, it was converted to calcium oxide only at temperatures above 500° C.; when the limed hide stippen was heated above 500° C., it lost weight comparable to the calculated weight of carbon dioxide. That the calcium is present as a carbonate agrees with the work of Rigot (4), who suggested that the cause of stippen is calcium carbonate formed in the grain of the skin.

If the chrome-tanned leather stippen analyses in Table I are examined, it is seen that magnesium and phosphorus play minor roles and that stippen is now a calcium salt. Although magnesium starts the trouble, it disappears from the condition, and calcium remains in the final leather. Since chrome-tanned leather is customarily pickled in a sulfuric acid solution, it is assumed that the calcium carbonate changes to the slightly soluble calcium sulfate and that the magnesium ammonium phosphate dissolves. The chrome-tanned leather stippen gave a very positive test for sulfate when tested with barium chloride. It is interesting to note that although stippen was originally thought to be one type of salt, the data in Table I indicate that the salt changes with the process and exists as three different salts.

Since there is evidence that the salt that crystallizes in the grain of salt-cured hide is magnesium ammonium phosphate, the next question that arises is: Where do the magnesium and other constituents come from? The analyses of various salts used in the curing of hides are given in Table II. It is of interest to note the amount of soluble magnesium and calcium in the various salts. The amount of calcium in the crystals does not vary much, but there is no doubt that the solar or marine salts contain a substantially

greater amount of magnesium than the rock salt. The rock salts which came from various mines in New York, Kansas, Michigan, and Louisiana contained less than 100 ppm of magnesium, but the solar salts evaporated in the West Indies (Area II), Massachusetts, and California contained more than 100 ppm: some contained as much as 1000 to 2000 ppm. The California solar salts that have been used on lots of hides which were found to have a high percentage of stippen contained 439, 680, and 1114 ppm. It is indicative from this table that the magnesium may come from the use of solar salt for curing.

TABLE II

AMOUNTS OF WATER-SOLUBLE MAGNESIUM AND CALCIUM IN VARIOUS SALT SAMPLES

Source	Magnesium ppm	Calcium ppm
Rock Salts		
Louisiana	trace	800
New York (I)	10	1650
Michigan	150	3610
New York (II)	12	2720
Kansas (I)	15	3560
Kansas (II)	15	4760
Solar Salts		
West Indies (I)	100	1750
Massachusetts	283	636
West Indies (II)	2720	2530
California (I)	439	870
California (II)	1114	840
California (III)	680	750

The origin of phosphate was then considered. The various salt samples were analyzed, and no salt, when new, contained phosphorus. Used salt or used brine did contain phosphate in a form that could be readily precipitated or determined colorimetrically. Apparently the blood and the tissues of the hide upon decomposing liberate phosphates. Post-mortem changes, warm storage, and prolonged storage promote autolysis and hydrolysis and consequently promote phosphate liberation. That the hide samples which contained stippen were not in the best state of preservation was confirmed by cross-sectional examination. The phosphate could originate from autolysis or from the reuses of salt.

The ammonia could be a breakdown product of the hide but more likely comes from manure which is embedded in the hair of the hide. This surface contamination could explain why the stippen forms only in the grain of the hide.

PRODUCTION OF STIPPEN

A gelatin solution to which was added a small amount of disodium hydrogen phosphate was prepared, poured into Petri dishes, and allowed to gel in the refrigerator. The gels were then removed, treated on the undersurface with a dilute solution of magnesium chloride, and replaced into the Petri dishes. The surface of each gel was treated individually with various ammonium salts and with fresh cow manure. After the plates remained about three days in the refrigerator, very definite star-shaped crystals formed on the surface of the gelatin. The best crystals formed in the plates treated with ammonium chloride and in those treated with manure. The crystals when isolated tested positive for magnesium, ammonia, and phosphate.

In an attempt to produce stippen during the salt-curing of hide samples, many conditions were tried. The following conditions seemed to be important:

1. Of the conditions tried, only hide samples allowed to stand two days at room temperature to promote degradation and phosphate liberation gave stippen formation.
2. Stippen formation occurred when magnesium chloride was a contaminant on the flesh side or the hair side; ammonium chloride, however, was tried only on the hair side.
3. Stippen could form when the hide was cured and stored in the refrigerator.
4. The samples which showed stippen had dehydrated to a certain degree during the curing period.

Stippen produced in hide samples in the laboratory and isolated from the stock after liming tested positive for magnesium, phosphorus, and calcium. That the crystals contained phosphate even though no phosphate was introduced to the system except by hide breakdown confirms that it is the phosphate of the hide itself that contributes to the formation of stippen.

STIPPEN CONTROL

In view of the mechanism above for the formation of stippen and the factors concerned, the matter of preventing stippen can be considered. Since salts containing magnesium are potential sources of the element which enters into the synthesis of an insoluble salt, the use of salts with more than 100 ppm magnesium should be avoided. As reused salt is contaminated

with blood, manure, and other chemical entities, it should be avoided; reused salt is not only concerned with stippen but is a liability to any good cure. Since a delay in cure allows for phosphate liberation, it is of the greatest importance to avoid this unnecessary carelessness. The holding of improperly cured hides contributes to degradation of the hide proteins and to dehydration; both are factors in the production of stippen and should be avoided.

There are a few suggestions as to how to remedy the condition when salts high in magnesium content are used. A sequestering agent may be added to the brine when brine-curing is being employed or may even be added to the salt when salt-curing is being done. The agent that may work is the disodium salt of ethylene diamine tetra acetic acid. According to Woodroofe (15) the addition of 2% boric acid to curing salt has aided materially in preventing the formation of crystals in the grain of sheepskins of New Zealand which may be similar to the stippen condition in this country. Cured hides which are suspected may be soaked back in water which has had a chemical added. A small quantity of some solvent for magnesium ammonium phosphate may be effectively used at this stage and may prevent the double salt from forming and further rupturing the tissues.

When stippen is not suspected and shows up in limed stock, the affected hides should be pickled in a hydrochloric acid solution instead of the conventional sulfuric acid solution. Whereas the calcium carbonate in the limed hide goes to calcium sulfate when sulfuric acid is used, it goes to the soluble calcium chloride when hydrochloric acid is used, and thus the hard crystals are eliminated. This latter suggestion is only a partial remedy, as there are no means of preventing the ruptured tissues from later filling with grease or some filling material and showing as pimples in the finished leather.

SUMMARY

The factors concerned with the formation of stippen are based upon the chemistry of the crystals and indicate that stippen develops in stock during curing. Its cause is primarily magnesium in curing salt; however, phosphate (a breakdown product of hide) and ammonia (present in manure) are also involved. Stippen changes during liming, becoming a double salt of magnesium ammonium phosphate and calcium carbonate, and changes again during pickling and tanning, becoming a calcium sulfate.

The methods to remedy the situation include:

1. Preventive measures:
   a. Avoid using salt which contains more than 100 ppm Mg.
   b. Avoid hide breakdown and the use of reused salt.
   c. Avoid long storage periods and dehydration during cure and storage.

2. Corrective measures:
   a. Use a sequestering agent with solar salt.
   b. Add a chemical to the soak water that will dissolve $MgNH_4PO_4$.
   c. Use an HCl pickle instead of the conventional H_2SO_4 pickle.

ACKNOWLEDGMENT

The data from a cooperating salt company and the damaged hide and leather samples from West Coast Tanners are gratefully acknowledged. The technical assistance of Mr. Ed Fugikawa and Miss Audrey Douglas has been important in completing the analyses and is sincerely appreciated.

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DISCUSSION

F. Leslie Collins (International Shoe Co., St. Louis): I thank you, Mrs. Tancous, for an excellent elucidation of one of our problems. Studies of this kind should pave the way for a reduction, or possibly a complete elimination, of some of our troubles.

DR. TURLEY (Rohm & Haas Co., Philadelphia): This was such an enjoyable paper, with so much commercial and practical application, that I wish to say so.

I think I am right when I say that in the United States we do not have so much trouble with salt stippen. Mrs. Tancous shows that we have the kind of salt cure that prevents that. However, it has been quite prevalent in skins in New Zealand. I have just returned from there. The German tanneries also have been complaining about salt stippen.

I would like to mention the method of curing which they are working on down there, possibly from the wrong premise. Mrs. Tancous's work may explain the reason for the success of the curing. Curing calfskins with the salt and the addition of boric acid seemed to show positive results in elimination of stippen when the skins were kept several months.

I would say that stippen has something to do with bacteria, and hence the boric acid was used. I was somewhat surprised that it was effective, because boric acid is not a very strong antiseptic. I wonder if Mrs. Tancous would feel that boric acid on the addition of magnesium ammonium phosphate would produce a combination that would prevent the formation of salt stippen. If we could cure this problem, it would be wonderful for the New Zealand and other calfskin industries. The salt they use down there comes from fairly near sources—in the South Pacific islands—and they are probably salts of high magnesium content.

MRS. TANCOUS: Your suggestion of boric acid is quite a good one, because acid is effective in dissolving the magnesium ammonium phosphate. We thought of quite a few solvents for stippen, but I think boric acid is probably the best one. I will be interested in trying it when I get back.

DR. TURLEY: That is a suggestion of Mr. Woodroffe of New Zealand.

MRS. TANCOUS: Has he tried it?

DR. TURLEY: Yes, and in process it proved to be very positive.

MRS. TANCOUS: I don't believe it is the bacteria he is avoiding but that he is dissolving or preventing the formation because of the acidity.

MR. RODDY (Tanners' Council Research Laboratory): We approached this problem on salt stippen because it also happens to be prevalen there in the United States, particularly from the standpoint of West Coast hides.

DR. FRANK W. PENAPINTO (William Amer Co.): Have you tried to create this condition artificially by actually using magnesium?

MRS. TANCOUS: Yes, we have. Mr. Roddy, would you like to comment on that?

MR. RODDY: Mrs. Tancous has applied an approach that is very similar to what we would normally use in the way of plating out bacteria, where we put one salt below the gelatin or agar and the other salt up on the surface, and place them in a refrigerator. Ultimately you get diffusion and formation of these stippen crystals in an artificial manner using gelatin or agar as a substrate instead of collagen.

MRS. TANCOUS: We ran chemical analyses on these crystals also, and they were the magnesium ammonium phosphate. Mr. Roddy did not mention that we put phosphate in the gelatin.

Research and Development in Scientific Documentation

The NSF Office of Science Information Service has prepared the fourth number of the report "Current Research and Development in Scientific Documentation." These reports, issued semiannually, cover research and development activities in the following categories: studies of information requirements and use, research on information storage and retrieval, research on mechanical translation, development of equipment for documentation work, and miscellaneous related research programs. This fourth edition. . . contains descriptions of 78 research and development projects. These represent the work of some 50 organizations and individuals. (Some are engaged in programs in more than one of the categories listed above). As reported, the greatest concentration of effort is found in the research on storage and retrieval with 33 descriptive statements. Equipment development and mechanical translation are next in number of projects, with 16 and 14 respectively.

Five foreign countries are represented among the statements. These are England, India, the Netherlands, France, and Israel.

Comments on the report and suggestions for increased coverage in future numbers will be welcome.

Copies of this report may be obtained from the Superintendent of Documents, Government Printing Office, Washington 25, D. C.

—*Science Information News*, April-May, 1959. National Science Foundation, Washington, D. C.

The Office of Technical Services, U. S. Department of Commerce, announces that it is expanding the section, Translations in Process by Government Agencies, in the semimonthly publication *Technical Translations*, to include those in process by private firms and publishers. Translating groups in this category are invited to contact the Office of Technical Services, Department of Commerce, Washington, D. C., for additional information. Material to be indexed will be actually in process and not just contemplated. It may be in the form of books, monographs or articles, but it must be at least fifty pages in length.

THE DIFFERENT EFFECTS OF THE SORPTION OF CALCIUM AND OF SODIUM IONS ON THE SWELLING OF HIDE COLLAGEN*

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ABSTRACT

Swelling of hide collagen and the absorption of calcium and sodium ions by hide collagen reach equilibrium levels in very short time intervals. Therefore, measurements of these phenomena can be made before secondary changes occur in the collagen. Quantitative measurements of the amount of calcium and sodium absorbed indicate that calcium ions are more firmly bound than sodium ions and that calcium ions have a limited absorption, while sodium ions appear to be absorbed in the multilayer water of hydration. The concentration of sodium ions in this bound water appears to be closely related to the concentration of the sodium ions in the surrounding solution. Increasing the salts present in the multilayer bound water increases the degree of swelling. The calcium ions bound on specific sites do not have much effect on swelling in these solutions containing sodium ions.

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INTRODUCTION

The importance of lime treatments to the leather and gelatin industries has stimulated a vast amount of research on the effect of lime and lime with various additives on hides and purified collagen. Many of these studies were reviewed recently by Lollar (1). The swelling phenomena of collagen were also critically reviewed by Gustavson (2). Some of the most elaborate and interesting studies have been reported by Bowes and Kenten (3–7). These workers have studied the swelling of collagen under both acid and alkaline conditions, employing different acids and bases, and including the influence of added salts on the swelling produced by these reagents.

There appears to be a considerable difference in the degrees of swelling produced by sodium and calcium hydroxides at comparable alkalinities.

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The swelling in lime solutions is considerably less than in sodium hydroxide solutions even when allowance is made for the bivalent nature of the calcium ions (7). The effect of neutral salts added to lime solutions is also different from the effect when the same salts are added to sodium hydroxide solutions. When sodium chloride is added to sodium hydroxide solutions, the swelling effect on collagen is decreased (6). In contrast to this the addition of sodium chloride to lime solutions produces an increase in the swelling action (4).

These observations indicate that there must be some difference in the mode of action of calcium and sodium ions on the swelling phenomena of collagen. The previous studies have been concerned mostly with the relationship of the composition of the solution to the swelling phenomena. The present study is concerned chiefly with the relationship of the ions absorbed to the swelling phenomena. Because of the apparent difference in action between calcium and sodium ions, some experiments were arranged to study their behavior when they were in a competitive situation, and the change in the ratio between the ions in the solution and the ions absorbed in the collagen was determined.

EXPERIMENTAL

Preparation of collagen.—Fresh hides were washed with water and 8% salt solution, fleshed, clipped, and split to obtain the center layer. The center layer was then extracted three times each with 8% salt, acetone, water, half-saturated lime water, water, dilute acetic acid, water and acetone. The air-dried pieces were cut into thin shreds with a paper cutter. They contained 18.1% nitrogen, 0.65% amide nitrogen (3.6% of the total nitrogen), and 13.6% moisture. There was 0.045 millimoles of calcium and 0.046 millimoles of sodium in each gram of dry collagen.

Swelling studies.—Two grams of the air-dried shreds were weighed in a covered Petri dish and then put into a covered glass dish containing 50 ml. of the lime or sodium hydroxide solutions, or 100 ml. of the salt-containing solutions. At completion of the swelling period the shreds were removed from the solution, blotted twice on clean cotton towels, placed in the covered Petri dish in which they were originally weighed, and weighed to determine the increase in weight. The increase in weight plus the weight of water originally present in the air-dried shreds was used to express the moisture of the swollen sample. The swelling data are, therefore, expressed as grams of water per grams of moisture-free collagen.

The swelling studies in salt solutions were all of one-hour duration, and 100 ml. of the salt solution was used. Where the studies were performed at pH 12.0 the pH was adjusted continuously throughout the run by adding 1*N* sodium hydroxide from a burette. The pH was determined with a high-alkalinity glass electrode calibrated at pH 12.5 with a suspension of calcium hydroxide.

For the few solutions containing only calcium salts the adjustment to pH 12.0 was made using lime water in place of the 1*N* sodium hydroxide so that these solutions would be free of sodium ions.

Analysis of lime and sodium hydroxide solutions.—Ten ml. of the solution remaining after the removal of the shreds was titrated with 0.1*N* hydrochloric acid to determine the concentration of lime or sodium hydroxide remaining. The original volume of solution minus the volume absorbed (measured by the increase in weight of the shreds) times the concentration of the final solution was used as a measure of the lime or sodium hydroxide not absorbed by the shreds. The difference between this quantity and the quantity added was considered a measure of the amount absorbed by the collagen.

Twenty ml. of the residual solution was analyzed for nitrogen by a semimicro Kjeldahl procedure. The total amount of nitrogen extracted was calculated from the result of this analysis and the calculated volume of the residual solution.

Analysis of the salt solutions.—Calcium was determined by a Versene titration method (8). Ten ml. of the solution remaining after the shreds had been removed was transferred to a 3-inch casserole and adjusted to approximately 100 ml. Two ml. of 10% potassium cyanide was added, and the solution was adjusted to pH 12.5 with 10% potassium hydroxide. Then 200 mg. of Cal Ver II indicator was added, and the calcium was titrated with a standard solution of disodium dihydrogen ethylenediamine tetraacetate.

Sodium was determined by the uranyl zinc acetate method (9). One ml. of the solution to be analyzed was added to 15 ml. of the zinc uranyl acetate reagent and, after standing, the precipitate was filtered off in a sintered glass crucible, washed according to the method, dried, and weighed.

Analysis of treated collagens.—The blotted and weighed shreds from the swelling experiments were put into large platinum dishes and ashed at 600°C. for four hours. The ash was dissolved in a small amount of hydrochloric acid and made to 25 ml. volume, and aliquots of this solution were used for the calcium and sodium determinations previously described. The recoveries of both calcium and sodium varied between 98% and 102% of the amounts added.

RESULTS AND DISCUSSION

Previous studies of the swelling phenomena of lime and sodium hydroxide have tried to simulate actual tannery conditions as to time and composition of the solutions. No studies have been reported where the treatment was less than three days. The data of Table I show that the swelling of collagen produced by both dilute sodium hydroxide and lime water solutions reaches

TABLE I

LIME- AND ALKALI-SWELLING OF COLLAGEN

Solution	°C.	Grams Water/Grams Dry Collagen after 1 hr.	2 hr.	4 hr.	17 hr.	24 hr.
Water	25	1.59	1.60	1.59		
0.1% NaOH	25	2.62	2.80	2.81	2.83	
Half-saturated $Ca(OH)_2$	25	1.92	1.90	1.94		1.86
Saturated $Ca(OH)_2$	25	1.98	2.04	2.04		2.05
0.1% NaOH	8	2.56	2.77	2.63	3.04	
Half-saturated $Ca(OH)_2$	8	2.12	2.01	2.06		2.18
Saturated $Ca(OH)_2$	8	2.12	2.12	2.19		2.08

an equilibrium value within one or two hours. The equilibrium value is maintained for at least 24 hours. It is also quite apparent that the lime solutions do not cause as much swelling as the sodium hydroxide solution. This agrees with the observations of Bowes and Kenten (4, 6) for experiments of longer duration. Furthermore, while the swelling produced by sodium hydroxide is decreased slightly by lowering the temperature, the swelling produced by lime solutions is increased slightly by lowering the temperature.

The half-saturated lime solution was originally almost equivalent to the sodium hydroxide solution in basicity, while the saturated lime solution contained almost the same concentration of calcium ions as the sodium hydroxide solution contained sodium ions, that is, the saturated lime solution had almost twice the basicity of the sodium hydroxide solution. However, due to the absorption of the reagents from the solution, reported in Table II, the

TABLE II

ABSORPTION OF ALKALI AND LIME BY COLLAGEN

Solution	°C.	Milliequivalents/Gram Dry Collagen after 1 hr.	2 hr.	4 hr.	17 hr.	24 hr.
0.1% NaOH	25	0.27	0.25	0.23	0.24	
Half-saturated $Ca(OH)_2$	25	0.37	0.42	0.45		0.90
Saturated $Ca(OH)_2$	25	0.63	0.57	0.61		0.95
0.1% NaOH	8	0.26	0.27	0.27	0.28	
Half-saturated $Ca(OH)_2$	8	0.35	0.39	0.39		0.39
Saturated $Ca(OH)_2$	8	0.51	0.49	0.51		0.52

equilibrium concentrations of these solutions were not directly comparable. The concentrations of the equilibrium solutions and of the original solutions at zero time are given in Table III. The 24-hour calcium absorption figures

TABLE III

CONCENTRATION OF REMAINING SOLUTION

Solution	°C.	Milliequivalents per Liter after 0 hr.	1 hr.	2 hr.	4 hr.	17 hr.	24 hr.
0.1% NaOH	25	25	17	18	19	19	
Half-saturated $Ca(OH)_2$	25	22	10	8	7		7
Saturated $Ca(OH)_2$	25	44	24	27	25		12
0.1% NaOH	8	25	18	17	17	17	
Half-saturated $Ca(OH)_2$	8	22	12	9	9		9
Saturated $Ca(OH)_2$	8	44	29	30	29		28

for the lime solutions at 25° are high because of precipitation of some of the calcium by atmospheric carbon dioxide. The data of these two tables show emphatically that calcium is bound to collagen much more abundantly than sodium even from solutions of considerably lower concentration.

The nitrogen solubilized by these solutions in the short times allotted are shown in Table IV. There appears to be a slight amount of nitrogenous

TABLE IV

NITROGEN SOLUBILIZED

Solution	°C.	Milligrams Nitrogen/Grams Dry Collagen after 1 hr.	2 hr.	4 hr.	17 hr.	24 hr.
0.1% NaOH	25	0.21	0.34	0.86	1.15	
Half-saturated $Ca(OH)_2$	25	0.28	0.33	0.45		0.75
Saturated $Ca(OH)_2$	25	0.37	0.45	0.52		0.87
0.1% NaOH	8	0.20	0.19	0.23	0.36	
Half-saturated $Ca(OH)_2$	8	0.10	0.13	0.21		0.37
Saturated $Ca(OH)_2$	8	0.09	0.22	0.28		0.45

material which is extracted very rapidly and may represent noncollagenous materials still remaining in the purified collagen. There is also a continuous increase in the amount of nitrogenous material solubilized as time proceeds. This probably indicates that changes are occurring in the collagen, although they have not proceeded to the extent that they influence the absorption of water or metals from the solution.

The differences in the absorption of calcium and sodium ions make it difficult to obtain their effects under comparable conditions, for if the solution concentrations are kept equal, the amounts absorbed are different; and

if the amounts absorbed are made equal, then the solutions must be of different concentrations. Neither of these situations could give comparable results for phenomena such as swelling where the result might depend both upon the solution and the materials absorbed. Swelling phenomena have usually been studied in relation to the concentration of the solution in equilibrium with the collagen, and the relationship of the materials absorbed has been studied only in incidental fashion.

TABLE V

EFFECT OF SALTS ON SWELLING OF COLLAGEN AT pH 7.0

Ionic Strength	Swelling*	Solution Analysis			Solids Analysis		
		Calcium†	Sodium†	Ratio**	Calcium‡	Sodium‡	Ratio**
0.20	1.68	0.036	0.088	0.41	0.113	0.109	1.04
0.21	1.75	0.027	0.126	0.21	0.096	0.169	.57
0.22	1.81	0.018	0.169	0.11	0.084	0.239	.35
0.17	1.89	0.049	0.026	1.88	0.137	0.020	7.00
0.19	1.81	0.041	0.064	0.65	0.124	0.056	2.22
0.20	1.79	0.033	0.096	0.35	0.109	0.102	1.07
0.35	1.80	0.099	0.053	1.86	0.209	0.048	4.36
0.38	1.82	0.083	0.129	0.65	0.201	0.161	1.25
0.40	1.90	0.067	0.199	0.34	0.180	0.271	0.66
0.39	1.75	0.072	0.172	0.42	0.191	0.244	0.78
0.41	1.83	0.054	0.252	0.21	0.160	0.332	0.48
0.44	1.81	0.036	0.335	0.11	0.124	0.495	0.25

*Grams of water per gram of dry collagen
†Moles per liter of solution
‡Millimoles per gram of dry collagen
**Calcium to sodium ratio

The data of Tables V and VI were obtained from experiments designed to determine the effects of calcium and sodium ions on the swelling of collagen under competitive conditions using solutions of approximately equal ionic strength so that the electrical properties of the systems would be as constant as possible. The ionic strength for the solutions used here is one-half the sum of each ion concentration times the square of the valence of the ion.

$$\mu = \tfrac{1}{2} [4 (Ca^{++}) + (Na^{+}) + (Cl^{-})]$$

This adjusts the solution to account for the stronger electrical effects caused by the divalent calcium ions. The ionic strengths reported were calculated using the concentrations found by the analysis of the solutions after equilibration. Two levels of ionic strength, 0.2 and 0.4, were used for the experiments at neutrality, and a 0.25 level was used for the experiments at pH 12.0.

TABLE VI

EFFECT OF SALTS ON SWELLING OF COLLAGEN AT pH 12.0

Ionic Strength	Swelling*	Solution Analysis			Solids Analysis		
		Calcium†	Sodium†	Ratio**	Calcium‡	Sodium‡	Ratio**
0.01	2.52		0.009			0.116	
0.13	1.93	0.042			0.278		
0.17	1.94	0.056			0.305		
0.24	1.99	0.080			0.342		
0.24	2.05	0.066	0.046	1.43	0.339	0.096	3.53
0.25	2.05	0.055	0.084	0.65	0.298	0.162	1.84
0.26	2.33	0.026	0.177	0.15	0.219	0.413	0.53
0.26	2.61		0.260			0.850	
0.29	2.79		0.287			0.914	
0.51	2.62		0.513			1.387	
0.07	2.67		0.067			0.400	
0.12	2.64		0.116			0.507	
0.17	2.59		0.168			0.623	

*Grams of water per gram of dry collagen
†Moles per liter of solution
‡Millimoles per gram of dry collagen
**Calcium to sodium ratio

Tables V and VI show that the ratio of calcium to sodium is always greater in the collagen than it is in the solution, indicating that calcium is bound more abundantly than sodium. Figure 1 shows that the amount of calcium

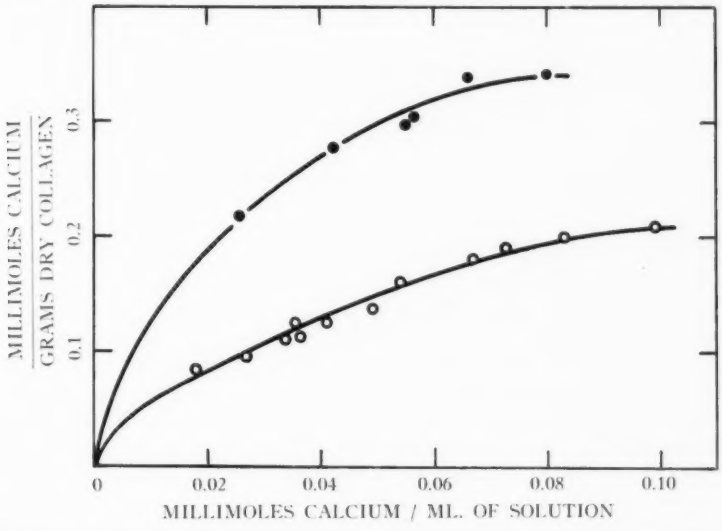

FIGURE 1.—Absorption of calcium by collagen in the presence of sodium chloride. ○, at neutrality; ●, at pH 12.0.

absorbed from these solutions increases with increasing calcium content of the solution except at the higher calcium concentrations, where there appears to be a limitation of the amount of calcium bound by the collagen. The amount of calcium bound at pH 12.0 is considerably greater than the amount bound at pH 7.0, but here again there appears to be a limitation to the amount of calcium bound at high solution concentrations.

The binding of sodium ions by collagen in the neutral solutions does not give the typical parabolic absorption but rather gives a straight line relationship (Fig. 2) of all the points extending from very low concentrations to

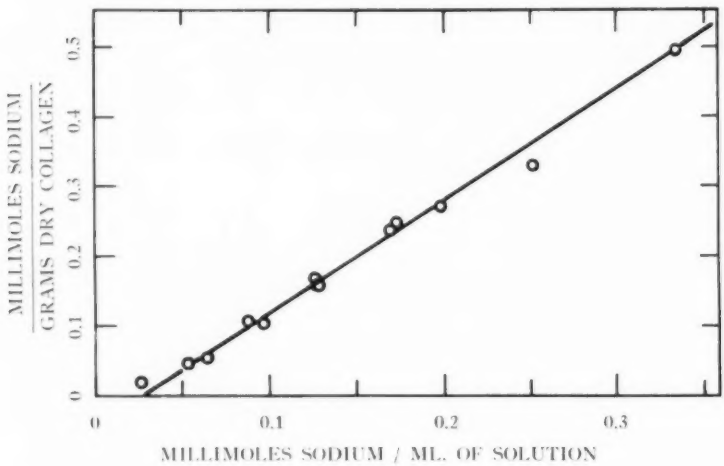

FIGURE 2.—Absorption of sodium by collagen at neutrality in the presence of calcium chloride.

very high concentrations. The slope of this line indicates that the millimoles of sodium absorbed per gram of collagen is 1.5 times the millimoles in one ml. of the solution, or in other words, the amount absorbed is the amount in 1.5 ml. of the solution. One gram of the collagen absorbs an average of 1.8 g. of these solutions. Therefore, it appears that possibly only about 0.3 g. of the absorbed water is bound to the collagen by primary linkages and does not contain dissolved salts. The remainder absorbs sodium ions approximately in equilibrium with the surrounding solution. The 0.3 g. of bound water is approximately equal to the amount found by Rougvie and Bear (10) at the second inflection point of the water vapor-absorption isotherm for collagen. This is the region of the curve where multilayer absorption of water begins to have its effect.

The present data do not indicate whether any of the calcium absorbed is located in the multilayers of sorbed water, although its presence there might be expected. If the amount of calcium present in 1.5 ml. of the neutral solutions is deducted from the amount absorbed, the remainder, which varies between 0.06 and 0.08 millimoles of calcium per gram of moisture-free collagen, could be considered the specifically bound calcium. This treatment of the data, however, cannot explain the limitation of the calcium binding at high calcium concentrations.

Ionic strength is not an important factor in controlling the sorption of calcium or sodium ions from neutral solutions, for both the 0.2 and 0.4 ionic strength points lie on a single smooth curve. The nearness of these solutions to the isoelectric point, 8.3, of this collagen preparation may account for this lack of effect. Here it must be remembered that although the net charge is zero at the isoelectric point, the total charge on the collagen is close to its maximum, and ionic interactions can exist.

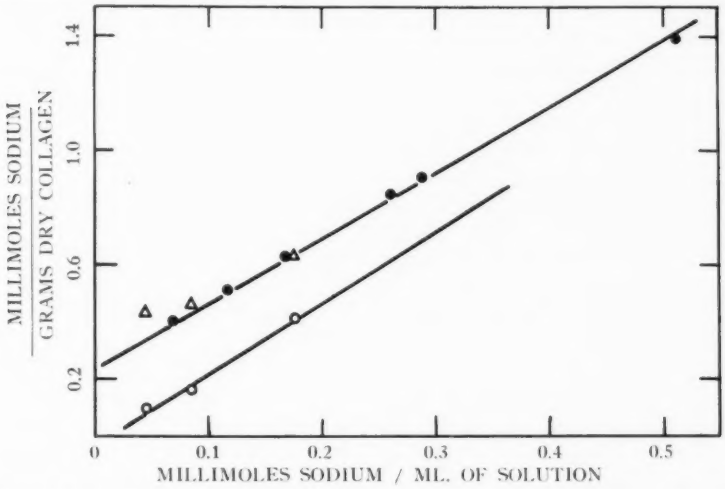

FIGURE 3.—Absorption of sodium by collagen at pH 12.0 in the presence of calcium chloride. ○, sodium values for mixed solutions; ●, sodium values for solutions containing only sodium cations; △, sodium plus calcium values for mixed solutions.

The plot (Fig. 3) of the sodium concentration in the solids versus the sodium concentration in the solutions at pH 12.0 shows two straight lines. The upper line traces points obtained from solutions containing only sodium cations. The lower line traces points obtained from solutions containing both calcium and sodium ions. The points on the upper curve designated with triangles were obtained by adding the millimoles of calcium absorbed to the millimoles of sodium absorbed which are shown on the lower curve.

These data have been interpreted as showing that there is a competition between calcium and sodium ions for certain specific sites on the collagen molecule. Calcium ions are more strongly bound than sodium ions, and if sufficient calcium ions are present, very few sodium ions will be specifically bound. The sodium concentration of the mixed solutions multiplied by the volume of the solution absorbed gives almost identically the total amount of sodium ions absorbed from these solutions. Therefore, it appears that most of the sodium ions absorbed from these mixed solutions are in the multilayers of absorbed water and that very few sodium ions are specifically adsorbed on the collagen.

Similar calculations with the calcium ion contents show that the amount of solution absorbed can contain no more than about a third of the calcium absorbed. Most of the calcium ions are, therefore, specifically adsorbed on the collagen.

In the absence of calcium ions more sodium ions are absorbed at the same sodium ion content of the solution. Therefore, the presence of adsorbed calcium ion prevents the specific adsorption of sodium ions. The triangular points of Fig. 3 show that the number of sodium ions prevented from adsorbing is almost numerically equal to the number of calcium ions adsorbed. It has already been shown that most of the calcium ions are specifically adsorbed. Therefore, most of the calcium ions are replacing sodium ions, ion for ion, and consequently only one of the two charges on the calcium ion is necessary for the binding of calcium ions by collagen. This would establish two significant points. The negative charges of collagen to which the positive ions are adsorbed are too widely separated to enable one calcium ion to satisfy two of them, and the binding of calcium ions by the negatively charged groups of collagen introduces positive charges in these areas which should change the electrical properties of the molecule.

The concentration of calcium ions in saturated lime solutions is not sufficient to supply the maximum amount of calcium that can be bound by collagen. Therefore, the addition of calcium chloride to lime solutions could produce the increase in swelling described by Vowes (4) through the introduction of additional bound positive charges which by repulsion of the existing positive charges could open up the protein to the penetration of more water.

The present experiments indicate that this effect is probably counteracted by the presence of sodium salts or the lower pH used, for in Table VI there appears to be little variation in the swelling of collagen for those solutions containing the varying concentrations of calcium. Figure 4 shows graphically that while there is little dependence of swelling upon the calcium content, there is a gradual increase in swelling as the concentration of sodium chloride is increased. However, there appears to be a limitation even on the sodium salt effect at moderate salt concentrations.

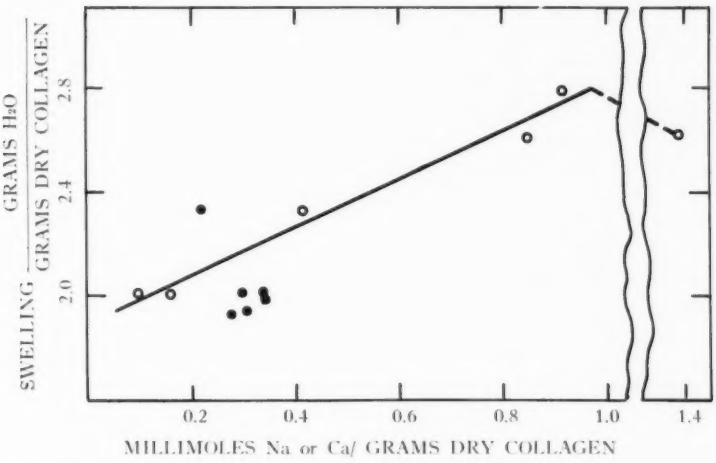

FIGURE 4.—Effect of absorbed salts on swelling of collagen at pH 12.0. ○, sodium values; ●, calcium values.

CONCLUSIONS

1. At neutrality and pH 12.0 there is a limited specific adsorption of calcium ions by purified hide collagen.

2. The specific adsorption of calcium ions is competitive with the specific adsorption of sodium ions on a molar basis.

3. The specific adsorption of calcium ions is stronger than the specific adsorption of sodium ions, and therefore, the calcium ions monopolize most of the sites for the specific adsorption.

4. In the presence of an adequate number of calcium ions the sodium ions appear to be chiefly in the multilayers of sorbed water which are at equilibrium with the surrounding solution.

5. In solutions containing both sodium chloride and calcium chloride at pH 12.0 the swelling appears to be independent of the bound calcium but increases directly with increases in the amount of bound sodium.

6. Since calcium and sodium ions compete on a molar basis, only one charge from the calcium ion can be involved in the adsorption process; therefore, the negative binding sites of collagen must be separated sufficiently that two of them cannot bind the same calcium ion to form a bridge type of linkage.

7. The adsorption of calcium ions on the negative binding sites of collagen will transform these sites into positive ones and thus change the electrical properties of the collagen.

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DISCUSSION

Dr. Robert M. Lollar (Armour Leather Co., Chicago): There are a couple of points that I wish to emphasize.

First, we should recall, as Dr. Mellon said, that this work was done on shreds of collagen under ideal conditions, and we should not, therefore, allow those ideal conditions to confuse our thinking with reference to the rapidity with which the attainment of equilibrium was found to occur in this work in comparison with our experience in the processing of skins and hides in the intact form.

However, I was rather interested in your observation, Dr. Mellon, that the calcium functions monovalently. It makes me think of some of the practical problems which one encounters—for instance, the case of the heavy neck area of skins and hides, where, because of slightly short bating and pickling, one may find streaks of lime present in the stock as it goes into tannage, and the resistance which these areas have to tannage.

From your observation that the calcium functions monovalently, these areas would contain positively charged protein carboxy groups which would give you the same charge as would be present in the chromium complex in many of your liquors. This idea furnishes a new interpretation for some of the difficulties one sometimes encounters in tannage.

Two questions occur to me: On the basis of the total nitrogen and amide-nitrogen analyses that were presented it is rather evident that the collagen used is a fairly pure collagen. Were analyses performed on these collagens to find the content of amino sugar that was present?

Second, observations were made in the paper on the solubilization of the protein and you mentioned in your discussion the effect of longer times in

the solutions on the deterioration of the collagen. Would you care to hazard a guess as to whether any hydroxyproline, for example, might be solubilized during this time?

DR. MELLON: We did not determine any of the amino sugars on this preparation. We have done it on similar preparations, however, and there are very slight traces in them. I don't think they are great enough to affect the values which we have presented.

In the paper we are presenting some additional data which show the amount of nitrogen which is solubilized in these solutions of lime and sodium hydroxide. The amount of nitrogen liberated seems to increase gradually with time. We believe this is a measure, somewhat, of deterioration or solubilization phenomena occurring in these solutions.

There is quite a rapid initial increase in the soluble nitrogen. You get a curve which comes up rapidly and then has a gradual slope, the sharp rise occurring within the one-hour period. We have a feeling that that is the removal of some nitrogenous material—not necessarily non-collagenous material. It could be collagen which has been partially degraded to gelatin as a result of our purification process. We rather feel that the longer you keep collagen in water, the more nearly you transform the collagen toward gelatin.

We regret that we did not perform hydroxyproline determinations on these solutions, so we cannot confirm whether this actually is solubilization of collagenous material or extraction of materials which we did not remove in the purification process, although the purification process did include extractions with salt solutions and half-saturated lime solutions.

In this respect the product we were working with did have a slight content of calcium and sodium ions, and these amounts have been included in the values which we have calculated as absorption.

Now, on continuous washing of these absorbed materials, all the sodium and calcium ions will be removed. It takes a considerably long washing period to remove the last residual traces, but I feel quite confident that most of it could be washed out if a sufficient length of time were given and a sufficient number of changes of solution. So we do feel this absorption is completely at equilibrium.

JAMES M. CASSEL (National Bureau of Standards): I wonder about this suggestion that only one of the valences of calcium was being tied up with the carboxyl groups in the collagen. Has something of this same nature been verified with resins, where calcium has been shown to have only one of the valences tied to the ion exchange resins?

DR. LOLLAR: You are asking whether, if there are ion exchange resins with the carboxyl groups, calcium functions only monovalently. Dr. Mellon?

DR. MELLON: I have no experience with it, but I have not been looking for anything of that nature.

MR. CASSEL: It seems to me that there is an exact comparison.

DR. MELLON: It might be quite similar, yes.

DR. PETER R. BUECHLER (Rohm & Haas Co.): It was quite apparent that at neutrality relatively little calcium is absorbed in comparison with the calcium which is taken on at high pH's. However, the material used—if I recall correctly, having prepared similar materials at one time—has an isoelectric point of somewhere around 7.8. Therefore, at neutrality you are working on the acid side of the isoelectric point and you have repression of the carboxyl group ionization. Consequently, this would very definitely, I think, affect the absorption of calcium. I wonder if you are in agreement concerning this explanation.

DR. MELLON: I am not quite sure that it is the full explanation. By the time you have reached a pH of 7, most of the carboxyl groups should be fully ionized. Only a few of them would not be. We cannot deny that there is a difference due to pH, but I don't think our data are sufficient to show what it is at the present time.

Union Research Institute Chinese Index

The Office of Science Information Service has recently received a copy of the *Index to the Material on Communist China Held by the Union Research Institute*. This index is a translation of the Chinese index compiled by the staff of the Institute in Hong Kong, who have collected data from Communist Chinese newspapers, serials, and monographs since 1949. At the time of publication 700,000 clippings from some 100 mainland newspapers and 200 periodicals were available in microfilm.

The "science" category in the index is divided into general, anthropology, astronomy, geology, biology, mathematics, physics and chemistry, atomic energy, history, geography and others.

In the appendix which lists the Chinese and translated serial title, holdings, place and frequency of publication, there are 20 titles under "natural science", 53 under "technical" and 12 under "medicine and hygiene".

A photoduplication copy of this index and other publications of this Institute can be obtained from the Library of Congress, or photocopies of the original publications may be obtained by writing to the Institute at 110 Waterloo Road, Kowloon, Hong Kong.

—*Science Information News*, June-July, 1959. National Science Foundation, Washington, D. C.

THE EXTRACTABILITY OF COLLAGEN FROM HIDE POWDER TREATED WITH FORMALDEHYDE*

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ABSTRACT

Aging appears to induce a greater degree of cross-linking in collagen; consequently, its extractability from tissues should be reduced. To pursue this point a study was made of the extractability of collagen from hide powder as a function of the extent of treatment with formaldehyde at pH 7-8. The ultraviolet absorption was used to follow the extraction process; the possible role of lysine ϵ-amino groups in collagen stabilization was demonstrated. It also appeared that solubilization of collagen by acetic acid occurred because of a reaction between the solvent and the ϵ-amino groups of lysine. A relationship between the absorption (A), the extraction number (n-1), and an empirical constant (B) was found, i.e., Log A_n = log A_1 − (n-1) B.

INTRODUCTION

Collagen appears to undergo certain modifications in aging tissues. There are observed (*a*) a decrease in its swelling (1, 2), (*b*) a lesser ability to relax from a chemically induced state of contraction (3), (*c*) an increase in its thermal shrinkage temperature (4), and (*d*) a reduction in its extractability (5). The statement is made frequently that biological aging induces a greater degree of cross-linking in collagen. The aforementioned changes (*a–d*) suggest that this might be true because these results are achieved also when cross links are introduced into collagen by tanning (6, 7). The similarity in effects of natural aging and formaldehyde treatment (rat tail tendons) intimates the participation of basic amino groups.

This study was undertaken to ascertain the extractability of collagen as a function of degree of cross-linking of its basic groups. Formaldehyde was selected again as the cross-linking agent because its reaction with collagen (amino groups) is understood perhaps more thoroughly than other tanning reagents. Dilute and concentrated aqueous solutions of acetic acid were

*Presented at the 133rd Meeting, American Chemical Society, San Francisco, California, April, 1958.

used to extract protein from a tissue substitute, American Standard Hide Powder (8), after treatment with formaldehyde. The ultraviolet absorption spectra of the extracts were measured and found to be valuable in analyzing the cross-linking and the solubilization reactions. It is admitted that hide powder is not representative of "native" collagen, but its availability and freedom from gross amounts of extraneous tissue protein and polysaccharides make it suitable as a model tissue substance. Because of the necessary chemical treatment which the hide powder has undergone, collagen extracted from it is modified but not completely denatured.

EXPERIMENTAL

Formaldehyde treatment.—Two hundred-mg. samples of hide powder collagen were placed in screw-cap tubes of 15-ml. capacity. Dilutions of 37% formaldehyde (Formalin) were made up by adding the requisite volumes to a sodium acetate solution of pH 7.8 (10 g/100 ml). In this way 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4} and 10^{-5} dilutions of the original concentration of Formalin were prepared. Ten ml. of the diluted formaldehyde solutions were added to the hide powder and allowed to react for 15 minutes. The mixture was centrifuged, and the supernatant solution was discarded. The formaldehyde-treated residues were suspended in 10 ml of water and centrifuged again. The supernatant fluid was discarded, and the water wash was done a second time.

Successive extractions.—After formaldehyde treatment the samples were extracted at 6°–8° C. by shaking them for 24 hours with 5.0 ml. of 0.5*M* acetic acid. They were then centrifuged to pack the insoluble residue. The supernatant solution of treated collagen was removed, and new solvent was added in order to repeat the extractions. Four extracts of acetic acid–soluble components were obtained in this manner. The spectroscopic absorption (A) at 350 millimicrons wavelength was measured in a Beckman DK-2 spectrophotometer. A separate calibration showed that the absorption (A) of soluble collagen was related linearly to the nitrogen content determined by a micro-Kjeldahl analysis. The absorption also was related linearly to the collagen concentration (biuret analysis) after formaldehyde treatment.

Solubility in concentrated acetic acid.—Samples of collagen which had been treated with 10^{-2}, 10^{-3}, and 10^{-4} dilutions of Formalin were extracted four times each for 24 hours with 0, 20, 40, 60, 80, and 100% acetic acid. After centrifugation the supernatant solutions were analyzed spectroscopically.

Ultraviolet absorption spectra.—The UV spectra between 350 and 250 millimicrons were obtained on the collagen solutions of the formaldehyde-

treated samples as well as of the nontreated samples. The absorption at λ relative to that at λ = 350 millimicrons

$$\frac{A_\lambda}{A_{\lambda = 350}}$$

was plotted against λ. Data were obtained for cross-linked hide powder solubilized by dilute and concentrated acetic acid solutions.

RESULTS

Successive extractions.—The absorbances at 350 millimicrons (A) of the 0.5*M* acetic acid–soluble fractions of hide powder are analyzed in Fig. 1. The logarithm of A is plotted against the extraction number minus one

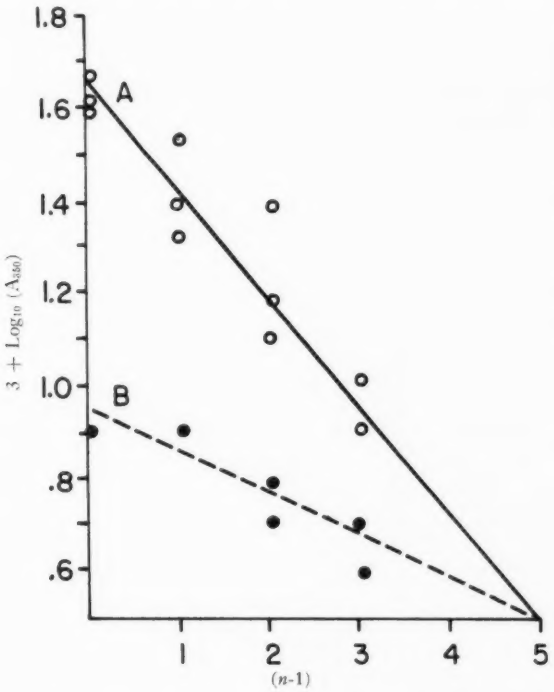

FIGURE 1.—The successive extraction of hide powder collagen with 0.5*M* acetic acid after treatment with formaldehyde solutions. pF = 5 for line A and 1 for line B. A = .00037% formaldehyde. B = 3.7% formaldehyde.

(n-1) for 10^{-1} and 10^{-5} dilutions of Formalin. The slope (B) of the linear regression equation, $\log A_n = \log A_1 - (n\text{-}1)\,B$, decreased as the concentration of the cross-linking reagent was increased. The slope (B) was evaluated and related to the dilution (F) of formaldehyde used in the treatment. The latter is expressed as $pF = -\log F$ where $F = 1$ ($pF = 0$) for a stock 37% Formalin. At $pF = 7$ the formaldehyde concentration was considered to be zero. Values of B ranged 0.10 to 0.23 while pF was varied from 1 to 7. B at $pF = 0$ was estimated to be zero. Thus, at high degrees of tanning the extractability is low, but less dependent upon the number of extractions than at lower degrees of tanning.

Let the quantity of collagen dissolved by the solvent during the four extractions be called Q. This can be evaluated by adding up the amounts of collagen dissolved in each of the four successive extracts, i.e.,

$$Q = \sum_{n=1}^{n=4} C_n V_n ,$$

where C_n is the collagen concentration (mg/ml) and V is the volume (ml.) of solution. However, the absorbance (A) of the solution was substituted

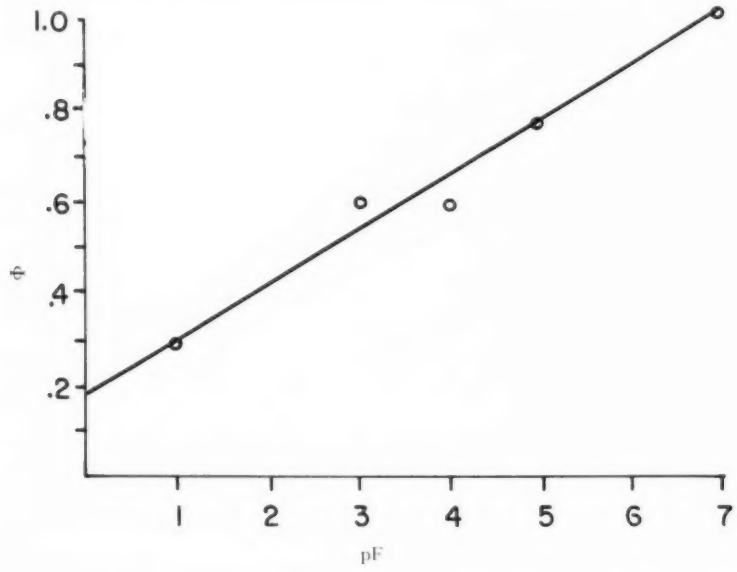

FIGURE 2.—Influence of concentration of Formalin upon quantity of collagen removed by four successive extractions with 0.5*M* acetic acid.

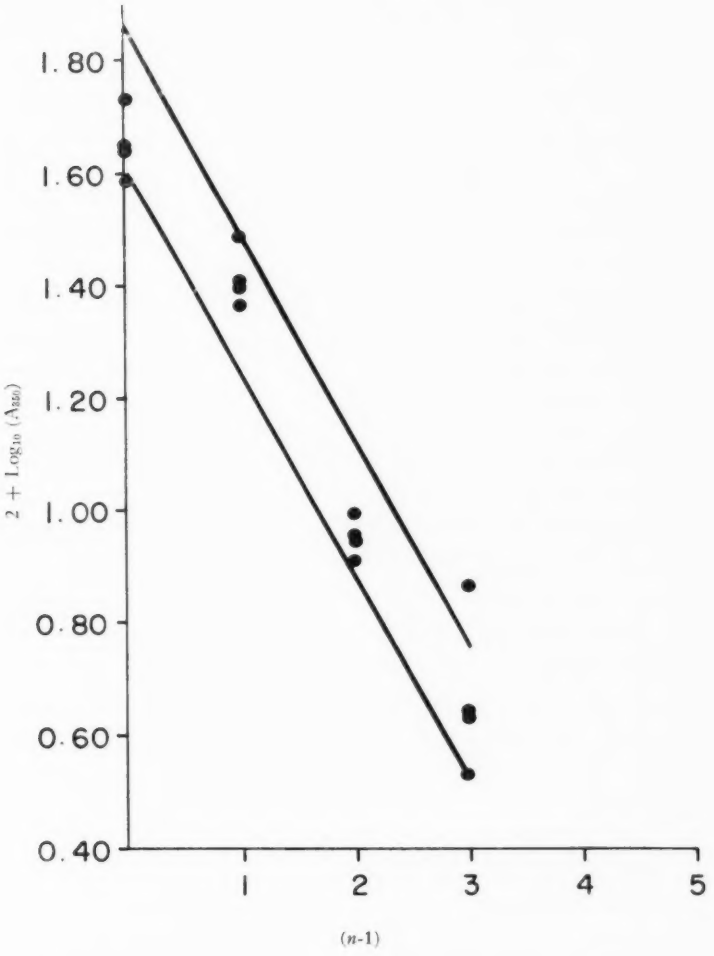

FIGURE 3.—The successive extraction of hide powder collagen with concentrated acetic acid. The data for 20, 40, 60, and 80% (volume) are bounded by the lines.

for C since the two are related linearly. The accumulated amount of collagen (Q) dissolved by acetic acid after treatment with formaldehyde of concentration F can be computed in terms of the absorbance and compared with

that for no treatment (F = 0, approximately, at pF = 7). The ratio of these amounts $\frac{Q_F}{Q_{F=0}}$ equals a function of the sum of absorbances. Thus,

$$(1) \qquad \frac{Q_F}{Q_{F=0}} \qquad \frac{\sum_1^4 A_{n,\,F}}{\sum_1^4 A_{n,\,F=0}} = \Phi$$

where the calibration constants and the volume terms cancel out of the ratio. Let us define a new term, Φ, according to the right side of equation (1), which will simplify the notation. Figure 2 shows that Φ was reduced linearly with decreasing pF.

Solubility in concentrated acetic acid.—In Fig. 3 there is shown an analysis of the absorbance of cross-linked collagen (pF = 3) based upon equation (1). The respective log A_n terms were nearly 10 times greater in value for concentrated acetic acid solutions than those obtained in 0.5*M* acetic acid. The slopes at 40, 60, and 80% acetic acid were the same, but the absorptions

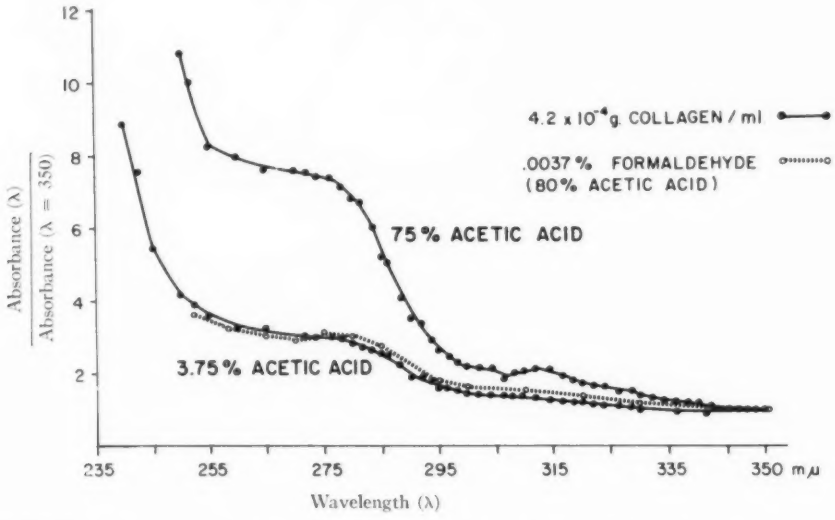

FIGURE 4.—The ultraviolet absorption spectra of soluble collagen in dilute and concentrated acetic acid solutions with free (———) and blocked (– – – –) amino groups of lysine.

are higher than at 20% acid. The absorbance at 0 and 100% acid was negligible. Linearity between log A_n and $(n\text{-}1)$ also was found for the samples treated at pF = 2 and 4. All the slopes were the same, but the absorbances for pF = 2 were lower than those of pF = 4.

Spectral properties.—The absorption ratio $\frac{A_\lambda}{A_{\lambda = 350}}$ of the acetic acid-soluble fraction was plotted against λ from 240 to 350 millimicrons. Figure 4 shows that the ratio is large (7–8) below 280 millimicrons in 75% acid, whereas in 3.75% acid it is smaller (2–3) for identical concentrations of untreated collagen. Cross-linked collagen in 80% acetic acid had an absorption curve coincident with the nontreated collagen in 3.75% acid. See Fig. 4.

DISCUSSION

The successive extraction of hide powder using 0.5 molar acetic acid at low temperature removed a "soluble" and possibly "modified" form of collagen. The residue after four extractions was resistant to further extraction and appeared to be distinctly "insoluble". The quantity of this acetic acid-soluble fraction depended upon the concentration of cross-linking agent (formaldehyde) used in the pre-extraction treatment. Furthermore, it was related to the concentration of acetic acid in the solvent.

The theoretical significance of B in the linear regression of log A_n upon $(n\text{-}1)$ is not completely clear. One factor which might influence B is the relative amounts of soluble and insoluble constituents present in the hide powder. In addition to this the individual solubility of each component might influence B. Chemical reaction between the solute (hide powder) and components of the solvent (water, acetic acid, H^+ ,Ac^-) would alter these solubilities. Therefore, the interpretation of B must wait for further studies to be completed.

At neutral pH lysine appears to be a residue of collagen whose ε-amino group is within easy access of formaldehyde (9) and water vapor (10). This steriochemical freedom increases the likelihood that it could be a site wherein new cross links form with aging. A normal amount of interhelical stabilization of collagen might occur here by hydrogen bonding as well. The fact that mineralization of soft and hard cartilage appears to involve the ε-amino group of lysine is evidence of its availability for chemical reaction (11).

It is plausible to view the reaction between collagen and acetic acid as occurring partly at sites of the ε-amino groups of lysine. Treatment with formaldehyde at slightly alkaline pH blocks a number of these groups, but a few probably remain free, since all are not in the correct steriochemical position for the establishment of a bridge between chains. The UV spectra

of Fig. 4 show that there is an interaction between the acetic acid–water solutions and some part of the extracted collagenous material. Since this interaction can be blocked by formaldehyde, as demonstrated by the data in Fig. 4, this suggests the participation of the ϵ = amino group of lysine in the collagen–acetic acid association.

SUMMARY

(*a*) Samples of hide powder collagen were treated with formaldehyde at pH 7–8 and successively extracted with acetic acid–water solutions. The quantity removed by 4 extractions decreased when the concentration of formaldehyde was raised.

(*b*) The extraction of hide powder by acetic acid solutions obeyed a simple relationship. This was found to be

$$\text{Log } A_n = \log A_1 - (n\text{-}1)\ B$$

where A_n is the absorption at 350 millimicrons (proportional to concentration) at extract n, A_1 is that at $n = 1$, and B is a characteristic slope.

(*c*) The ultraviolet spectral measurement suggested that acetic acid–water solutions dissolved the hide powder by associating with the ϵ-amino groups of lysine. This contention was supported by spectral measurements on hide powder in which the ϵ-amino group of lysine was blocked by formaldehyde.

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LIFE LINES

Brief Biographies of Our Contributors

Robert J. Boucek received his M.S. degree in phsyiology from the University of Minnesota (Mayo Clinic) and his M.D. from the University of Pittsburgh. He is now Senior Investigator at the Laboratories of Biochemistry, Howard Hughes Medical Institute, Miami, Florida, as well as Professor of Medicine, and Chairman of Section on Cardiology, School of Medicine, University of Miami, Coral Gables, Florida.

Dr. Harry R. Elden earned his B.S. in 1950 and his M.S. in 1953 from the University of Miami, where he majored in chemistry. In 1956 he received his doctorate at the Catholic University of America with a major in physical chemistry and minors in physics and physiology. From 1954 to 1956 he was a Commissioned Officer of the United States Public Health Service, National Institutes of Health, Bethesda, Maryland. Now he is an Investigator at the Laboratories of Biochemistry, Howard Hughes Medical Institute, Miami, Florida, and Assistant Professor, Department of Biochemistry, School of Medicine, University of Miami, Coral Gables, Florida. His primary research interests are the effects of biological aging upon physical chemical properties of connective tissue, the mechanism of bone formation, and biophysical aspects of degeneration of joint tissues.

Helen A. Gruber is a Chemist in the Composition Investigations of the Hides and Leather Laboratory of the Eastern Utilization Research and Development Division of the U. S. Department of Agriculture. She received the B.S. degree from Chestnut Hill College, and prior to her work for the Department of Agriculture she was engaged in the analysis of leather for the Philadelphia Quartermaster Depot.

Dr. Edward F. Mellon is Head of the Composition Investigations of the Hides and Leather Laboratory of the Eastern Utilization Research and Development Division of the U. S. Department of Agriculture. He received an A.B. degree from Allegheny College, his M.S. degree from the University of New Hampshire, and the Ph.D. degree from the Catholic University of America. He joined the staff of the Protein Division of the Eastern Regional Research Laboratory in 1942 and carried out research on the physical properties and structure of proteins. He transferred to the Hides and Leather Laboratory in 1954 to study the structure and reactivity of animal hides.

Dr. Fred O'Flaherty, Secretary-Treasurer of ALCA and a former president, has been a member of the Association since 1928 and a frequent con-

tributor to the *Journal* since 1930. He came to the University of Cincinnati in 1925 as research assistant, subsequently becoming research associate, Professor of Basic Science, and Director of the Tanners' Council Research Laboratory. Presently he is Administrator of University Research.

MRS. JEAN JACOBS TANCOUS holds both B.S. and M.S. degrees from the University of Cincinnati. Since 1949 she has been a Research Associate in the Tanners' Council Research Laboratory at the University, working chiefly on the microscopy and microbiology of skin and hide. She has contributed frequently to this journal.

SAMUEL J. VIOLA is a Physical Science Aid in the Composition Investigations of the Hides and Leather Laboratory of the Eastern Utilization Research and Development Division of the U. S. Department of Agriculture. Prior to 1954, when he joined the Hides and Leather Laboratory, he spent 13 years on various studies involving the milk proteins.

STEFANIE L. ZACHAR was graduated from Mills College in San Francisco in 1956 with a B.A. in chemistry. Since then she has been a research assistant in the Laboratories of Biochemistry, Howard Hughes Medical Institute, Miami, Florida.

Under a recent National Science Foundation grant, the Operations Research Group of Case Institute of Technology will analyze the reading done by two groups of research scientists during the time they devote to scientific communication. An earlier study by the same organization demonstrated the feasibility of applying operations research techniques in this field and showed that the average industrial chemist spends more time in scientific communication than in all the rest of his scientific activities combined. The data collected in that study indicated that in 1957 he read only about one-half of one percent of the articles published in chemistry. The approximately 300 observations which caught chemists reading journal articles involved some 71 different chemical journals. Because the chemists' total time was covered by the first study, these observations of reading constituted only a small fraction of the total (about 300 out of 25,000)

The new study will be limited strictly to reading time. The sample of scientists covered, however, will be expanded to include chemists and physicists in industry, government, and universities. The purpose of the investigation is to identify and analyze both what kinds of scientific material (journal papers, books, patents, abstracts) these scientists read and the reasons behind the reading—that is, whether for general technical information, for specific technical information, or for sources of information.

A second phase of the new study, to be conducted simultaneously with the first, will involve an economic analysis of scientific journal publication. Information will be gathered on publication costs of a representative sample of scientific journals. These data, combined with information on what is read, may make possible the determination of costs per page read.

—*Science Information News*, Vol. 1, No. 3, June-July, 1959, National Science Foundation, Washington, D. C.

ALCA NEWS

Proceedings, Reports, Notices, and News

of the

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POSITION WANTED—Tanner, 33 years old, is seeking position. Wide experience in charge of production as well as diversification and development of new lines. Married. College graduate. Speaks fluent Spanish. Willing to relocate. Available immediately. Reply to Box 128, c/o Secretary, American Leather Chemists Association, University of Cincinnati, Cincinnati 21, Ohio.

DR. HENRY B. MERRILL HONORED BY THE AMERICAN CHEMICAL SOCIETY

DR. HENRY B. MERRILL

We were glad to hear from the Milwaukee Section of the American Chemical Society that they had chosen Dr. Henry B. Merrill as the recipient of their 1959 Award. Dr. Merrill was cited for outstanding contributions and service to industry, the profession, and the section in the Milwaukee area. The award was presented in an impressive ceremony at the November 20th meeting. Dr. Merrill received a medal, a certificate, and one hundred dollars, the latter to be given to an institution of his choice for the purchase of books on chemistry. Dr. Merrill is the second recipient of this Award. We add the hearty congratulations of our members to Henry Merrill.

Dr. Merrill has served the American Leather Chemists Association in many capacities, most recently as Editor of our *Journal* from 1956 to 1959. He has been a member of the Editorial Board since 1948 and consented to continue in this capacity after completing the three-year term as Editor. He was our President from 1938 to 1940. He received the Alsop Award at the Golden Anniversary Meeting in 1953 for outstanding scientific and technical contributions to the leather industry.

Dr. Merrill has been a member of the ALCA since 1928. He has contributed over forty papers on leather chemistry and was a coauthor of a book *Analysis of Leather and Materials Used in Producing It.* He contributed the chapter on "The Mechanism of Unhairing" to Volume I of *The Chemistry and Technology of Leather.*

Dr. Merrill retired as Director of Research and Development at the B. D. Eisendrath Memorial Laboratory on October 1, 1959. He still acts as an abstracter for the ACS and reads many journals for articles on leather chemistry which he abstracts for *JALCA.*

Dr. and Mrs. Merrill are now enjoying poinsettias, gladioli, and sweet peas which are blooming in their yard in California. Their one problem is gophers that are converting their lawn "into a relief map of the Appalachian highlands." Poisoned grain only caused them to move from the back lawn into the front.

The Merrills' address is 7004 Schroll Street, Lakewood, California. We know they would be very glad to hear from their many friends and well-wishers.

EDITOR

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The above slate of candidates has been prepared by the Nominating Committee.

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Members note:

Additional candidates may be nominated by petitions signed by 15 or more active members. Such petitions shall reach the Secretary not later than April 1 and shall contain a statement of the willingness of the nominee to serve if elected. No member shall sign more than one petition for each office to be filled.

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Charles J. Cares, 31 Waverly Avenue, Lowell, Massachusetts.

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Paul E. Williams, A. C. Lawrence Leather Company, Division of Swift and Company, Newport, Tennessee.

CHANGES OF ADDRESS

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RESIGNATIONS

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Elmer H. Knoernschild, 803 North Third Street, Clinton, Iowa.

L. W. Morrow, A. C. Lawrence Leather Company, Newport, Tennessee.

John H. Ramsden, 32 Hampden Street, Swampscott, Massachusetts.

ABSTRACTS

Demetalization, Leveling, and Rechroming of Chrome-dyed Wool Pieces. H. E. Millson. *Am. Dyestuff Reptr.*, **48,** No. 18, 47–58 (1959).—A new method of demetalizing and leveling unevenly chrome-dyed woolen and worsted pieces is discussed. By treatment with a solution of a sequestering agent (tetra-sodium ethylenediaminetetraacetate), oxalic acid, and Na_2SO_4, salts of many metals (e.g., aluminum, copper, and iron) may be removed even after the dye-metal-wool complex has been formed. C.L.D.

Colour Index. Additions and Amendments. *Am. Dyestuff Reptr.*, **48,** No. 16, 32–42 (1959). C.L.D.

Recent Developments in the Chemistry of Wattle and Quebracho Tannins. D. G. Roux. *Das Leder*, **10,** 177–81 (1959); Editorial comment on the nomenclature of the parent substances of condensed tannins, 181–83.—A review lecture delivered in London. I.D.C.

Problems of Combination Chrome-Vegetable Tanning. Loss of Chrome in Vegetable Retanning. P. Erdi. *Das Leder*, **10,** 174–6 (1959).—Factors are listed which favor or retard leaching of chrome during retanning. The chrome loss was demonstrated by the fact that offal tanned with spent vegetable retan liquors contained 0.5% (collagen-basis) of Cr_2O_3 although it had been given no chrome tannin. Tests were made to determine if aging the chrome leather for periods up to 16 days before vegetable retanning would reduce leaching of chrome. Nine hides were tanned to contain 1% Cr_2O_3; then after various periods they were retanned in a 7°–9° Bé quebracho-Lignotan liquor, starting tannage with 1 day in a used liquor at pH 5.5–5.6. During aging, shrinkage temperature rose slightly from about 95° to a maximum of 98°. Data on Cr_2O_3 content of the leather showed a definite increase in stability only for some aging periods, for example, 16 days, but the data as a whole were inconclusive because of scattering of results. Washing in water for 1 day after the 6-day retanning period resulted in a considerable loss of chrome, indicating that the leather contained chrome-tannin complexes that could be washed out. Chrome pretanning increases takeup of vegetable tannin, and this greater degree of tannage can have a bad effect on grain appearance

and elasticity. It is therefore advisable to reduce the reactivity of the chrome leather by neutralizing it with a complex active agent such as sodium sulfite. A chrome-retan upper leather could not be taken directly from the chrome-pretan liquor to a strong vegetable liquor without an unfavorable effect on the grain; it was necessary to start the tanning in a used liquor. In one tannery where spent liquors could not be used, oiling the grain with a sulfonated oil emulsion 1 or 2 hours before retanning was effective in obtaining a uniform, bright grain surface. I.D.C.

Phthalate-masked Chrome Liquors. F. Kolos, *Das Leder*, **10,** 169–74 (1959).—Glucose-reduced chrome liquors, which produce full leather with a fine grain, contain principally oxalic and formic acid residues. Numerous other masking salts have been tried in an attempt to imitate glucose-reduced liquors. Formate-masked liquors penetrate well and produce leather with a fine, smooth grain, but leather which is somewhat flat. Acid masking agents which increase in the particle size of the chrome-tanning compounds and so increase affinity, produce firm, full leather but may cause drawn grain because of overtannage of the grain surface. Between these two extremes phthalate-masking is a good intermediate. These liquors produce full leather without drawn grain. To determine whether a chrome-alum liquor, comparable to a glucose-reduced liquor, could be made by masking with phthalate, a tanning experiment was conducted with the following 4 tan liquors: (A) *glucose-reduced:* 2400 g. $K_2Cr_2O_7$ and 2075 g. H_2SO_4 (96%) in 6200 ml. water at 90°C. reduced in 30 minutes with 720 g. glucose in 1000 ml. water; (B) *unmasked:* 8000 g. chrome alum in 25 (?) ml. water at 55°C. treated with 1150 g. Na_2CO_3 in 15 liters of water added in 20 minutes; (C) *phthalate-masked:* the same as B except that the alum was treated with 1500 g. Na_2CO_3 and 487 g. phthalic anhydride in 15 liters of water; (D) *phthalate-masked with glucose:* the same as C except that before neutralization 144 g. of glucose in 500 ml. of water was added. All solutions, after standing overnight, were made up to 50 liters; each contained 24.8 g. Cr_2O_3 per liter and had a basicity of 42.2–42.4%. Ten pickled calfskins were tanned with each liquor and then finished by the normal tannery processes. With liquor B there was a tendency toward loose grain and empty flanks. Leathers made with liquors C and D had fine grains, good feel, and decidedly full flanks. The leathers were split into 3 equal layers, and each was analyzed for Cr_2O_3 and fat. The average Cr_2O_3 content of the leathers was as follows: A, 5.23; B, 5.80; C, 5.58; and D, 5.69%. A value for uniformity of distribution of chrome or fat was calculated by dividing 100 times the analytical value for the middle layer by half the sum of the values for the 2 outer layers. Uniformities for Cr_2O_3, in the above order, were 73.2, 60.2, 73.5, and 76.5. For fat the uniformities were 26, 19, 37, and 24 resp. The results show that 0.4 mole of phthalate per mole of Cr_2O_3 gives satisfactory masking and makes a good tanning agent. Phthalate-masked liquors are simpler to prepare and are more reliably reproducible than glucose-reduced liquors. Phthalate is a divalent, chelate-forming radicle, but the increased particle size is compensated for by the decreased affinity. The velocity of the masking reaction was easily determined by cooling the solution at the end of a given time period to 0°C., shaking out uncombined phthalate with ether, evaporating the ether, dissolving the residue in water and titrating with phenolphthalein as indicator. Distribution of phthalate between water and ether was determined from a blank, and the coefficient so obtained was used to correct the data.

The coefficient was independent of basicity (pH) of the solution and progress of the reaction. With increasing basicity both the velocity of the reaction and the amount of coordinately bound phthalate increased. As basicity increased in the series 0, 25, 42, and 50% the amount of bound phthalate in 8 hours was 12.6, 30.2, 43.7, and 48.9% resp. of the amount present. With rise in temperature the velocity increased sharply. At 20°C. 43.7% of the phthalate entered the complex in 8 hours; at 55°C. 95% entered in 1 hour. I.D.C.

Technology of Sulfating Oils for Fatliquoring Leather. V. Pilc. *Kozarstvi*, **8**, 37–39 (1958).—Animal oils should be sulfated at 25°C., castor oil at 35°, and fatty acids from oxidized hydrocarbons at 35°–45°, and the temperature should be held constant by cooling. Sulfated products should be washed with 100% of a 40% solution of Na_2SO_4, at 35°C., maintained by heating. The used Na_2SO_4 solution may be diluted to 16°Bé, reused, diluted to 12°Bé, and used again. This is economical even though more NH_4OH may be needed for neutralization. See Czechoslovak Patent No. 84550. L.M.

Chrome Tanning in the U.S.A. L. Masner. *Kozarstvi*, **8**, 50–51 (1958). —A review of practical tanning in the U.S.A. L.M.

Criterion for Chrome Tanning. A. Blazej. *Kozarstvi*, **8**, 72–74 (1958). —Various factors have been proposed for calculating "chrome tanning substance" from Cr_2O_3 content, e.g., $Cr_2O_3 \times 2.73$ (Kubelka), $Cr_2O_3 \times 2.29$ (Zhemochkin), $(Cr_2O_3 \times 2.09) + 2.78$ (Kanagy). Chrome tanning substance was determined in dry Cr leathers by subtracting the sum of ash (less Cr_2O_3), fat, hide substance, and water solubles from 100. For leathers containing 4.8, 5.1, 4.2, and 5.5% Cr_2O_3, values of Cr tanning compound were 14.9, 12.9, 14.6, and 12.5%. If Cr_2O_3 is calculated on the hide substance basis, multiplication by 2.27 gives Cr tanning compound. This determination holds only for neutralized and unfinished leather, and it is needed only for calculating fixed tannin in Cr-vegetable leathers. L.M.

Influence of Leather on Polyvinyl Chloride Soles. Z. Stacke and A. Draticka. *Kozarstvi*, **8**, 42–47 (1958).—Yellow plasticized polyvinyl chloride (PVC) soles, stabilized with Pb stearate, sometimes turn dirty yellow. This has been traced to migration of polyphenols of vegetable tannins or syntans in the middle sole. The same change occurs with nonstabilized PVC, so Pb is not a cause. Films of PVC turn green to black after immersion in solutions of tannins or syntans and drying 48 hr. at 70°C. Syntans are more effective than vegetable tannins, but even the water solubles of sole leather can produce the discoloration. Migration of plasticizer from the PVC to the middle sole has been proved. Discoloration is hastened at high humidity (14 days at 100% R.H., 2 months at 65%), and humidity has more effect than rate of migration of the plasticizers. Discoloration is accelerated by oxidants and by atmospheric O_2, and is inhibited by the presence in the PVC of 2.5% $Na_2S_2O_3$, which has no adverse effect. The discoloration is not produced by Cr-vegetable or Al-vegetable middle soles. In white PVC middle soles pigmented with TiO_2, the discoloration is masked. Black rubber soles turn PVC middle soles a dark orange. Some dyes from upper leather can discolor PVC. Other shoe components, except shoe cartons containing leather fibers, have no effect. L.M.

Control of Bating by the Determination of the Enzymatic Activity of Bating Liquors. M. Radil, L. Dvoranek, and M. Madera. *Kozarstvi*, **8**, 11–14 (1958).—A modification of the Lohlein-Volhart method is used. The bate liquor is sampled after 5 min. and filtered. To 10 ml. of filtrate in a 100-ml. beaker add 20 ml. of 5% alkaline casein solution and digest 60 min. in a thermostat at 38°C. Add 10 ml. of a 15% solution of Na_2SO_4, filter the precipitated casein, and titrate 10 ml. of filtrate with 0.1*N* NaOH with cresol red to a light violet color. The test is repeated without digesting at 38°C. for 60 min., and the difference in ml. of 0.1*N* NaOH consumed is called the bating activity. In tests with 1 to 20 g. per liter of a commercial bate, the bating activity increased steeply to 16 g/l, above which the curve flattened out. A bate liquor aged 24 hr. at 38°C. retained 89% of its original activity. the effect of temperature in bating goatskins was studied, using 6.6 g/l of bate. The activity which was 0.62 at 38°C. fell to 0.43 at 25°C. after 24 hr. In a second experiment activities at 32°, 38°, 55°, 58°, and 60°C. were 0.55, 0.62, 1.1, 0.62, and 0.03. During normal bating of goatskins at a constant temperature of 37°C., the initial activity of 0.52 declined to 0.50 after 5 min., and to 0.21 after 120 min. if the skins were paddled, but only to 0.35 if paddling was omitted, showing that movement of the skins gives better utilization of the bating activity. L.M.

Properties of Collagen. V. Kubelka. *Kozarstvi*, **8**, 6–11 (1958).—Limed collagen is more susceptible to attack by trypsin or papain than is native collagen. The fibrils in the fiber bundles probably are bound together by chemical cross linkages as well as mechanically, which accounts for the slower attack on thicker bundles by enzymes. The nitrogen content of steer collagen is 18.0%, not 17.8%, and the correct collagen factor is 5.66 instead of 5.62. Water is bound in part as a dipole between -NH and -CO groups of peptides. The volume of a swollen collagen fiber is less than the sum of the volumes of collagen and water. Replacement of bound water by tanning materials converts collagen to leather. The shift in the isoelectric point from pH 7 to 5 as the result of liming is caused by splitting off of part of the diamino acids lysine and arginine. L.M.

Plastic Leather from Leather Fibers. R. Exner. *Kozarstvi*, **8**, 75–77 (1958).—Utilization of leather scrap for production of "plastic leather" is discussed. Plastic leather can be used for slipper soles, middle soles, and counters, but not for bottom soles or uppers. Chrome leather shavings, and cuttings and trimmings from vegetable sole, harness, and mechanical leathers are suitable raw materials. Vegetable cuttings usually are partially detanned with alkali. Plastic leather from vegetable leather has lower tear resistance but better stability of form than that from Cr leather. Cuttings from finished leather are not suitable. Plastomer or elastomer dispersions are suitable binders; nitrocellulose and Thiokol dispersions give a product with low wet-tear strength. Wet disintegration of the scrap is recommended. The length of the leather fibers should be 3–4 mm. Good-quality plastic leather contains 30–40% dry weight of binders. Polyvinyl acetate dispersions need 30% of plasticizer, usually dibutyl phthalate. The precipitation of binder on the leather fibers is usually done with $Al_2(SO_4)_3$ at 25°C. Vegetable scrap must be washed thoroughly as water solubles of vegetable leather stabilize the dis-

persion. Plastic leather of better mechanical properties is obtained by immersing the partly dried product in water at 70°C. for 2 hr. if plastomer dispersions have been used. Sometimes asphalt or paraffin dispersions are used to lessen the water absorption of the plastic leather. L.M.

Liming of Pigskins. V. Cik and V. Cerveny. *Kozarstvi*, **8**, 78–79 (1958).—The pigskin bend is very tight-fibered near the tail and loose near the head. This difference can be lessened by painting the back parts with 250 g. per l. of 60% Na_2S and 150–200 g. per l. of NaCl, piling for 24 hr., and liming for 1–3 days at 22°C. in 1200% water containing 15% Na_2S and 4.5% CaO on the dry weight. Painted bends may also be limed in 500% water containing 10% of 15% NaSH and 15% of 15% $Ca(SH)_2$ for 1–2 days, followed by 1–3 days in the sharp lime described above. It is also possible to immerse about the rear third of the bend in a solution containing 100–150 g. Na_2S and 100 g. NaCl per l. for 1–3 days, and then to lime the whole bend in a sharp lime; however, in this process the bend must be protected from putrefaction by a disinfectant. The addition to a lime containing 1200% water and 15% Na_2S, of 4.5, 9.0, 18.0, and 27.0% NaCl, on the dry weight of the bend, increased the thickness by 29.0, 31.2, 34.0, and 38.8% respectively. The most supple leather was obtained with the highest amount of salt. But when the same quantities of NaCl were added to liquors that contained 4.5% CaO in addition to the Na_2S the respective thicknesses were 43.0, 38.6, 37.8, and 31.2—just opposite to the trend in the previous experiment—and the leather from the liquor containing the most salt was least supple. The degree of liming depends on the time and temperature. Sharp, brief liming gives better and more supple bends. Dimethylamine liming was tried, without significant results. All pig bends must be degreased before liming, to obtain best results. L.M.

Chelometric Determination of Lime in Tannery Lime Liquors. A. Blazej and E. Markusovska. *Kozarstvi*, **8**, 117–20 (1958).—Centrifuge the lime liquor at 3000 rpm for 15–20 min. Dilute 25 ml. of the supernatant to 100 ml. with redistilled water, add 2 ml. of 2*N* NaOH, 5 ml. buffer, and 0.3 g. of dry Murexide, and titrate with 0.1*M* Komplexon III as previously described (see abstr., *JALCA*, **52**, 659 [1958]). Results compare favorably with those by precipitation as oxalate and titration with $KMnO_4$. Sole leather lime liquors gave the following results:

Total alkalinity (g. CaO/l.)	2.06	3.06	2.08	2.65	3.05
Chelometric method (g. CaO/l.)	1.57	2.16	1.71	2.18	2.40
Manganometric method (g. CaO/l.)	1.62	2.02	1.63	2.28	2.31

The maximum difference is 0.2 g. CaO per l., caused by the presence of 2.6–3.4% MgO in the lime used. Fe, Al, Mn, and Si do not interfere.
L.M.

The Determination of Magnesium and Calcium in Leather Ash by Titration. E. Markusovska and A. Blazej. *Kozarstvi*, **8**, 133–35 (1958).—Difficulties and differences in gravimetric determinations of Mg in leather ash are described. A chelometric method is recommended. Prepare (A) a 0.01*M* solution of Chelaton 3 (3.7225 g. per l.), (B) a buffer containing 107 g. NH_4Cl and 710 ml. NH_4OH in 1 liter, and (C) a precipitating solution

containing 140 g. NH_4Cl, 6 g. $(NH_4)_2C_2O_4$, and 14 ml. NH_4OH in 1000 ml. Dissolve the ash from 3–4 g. vegetable leather in 25 ml. HCl (1:4), filter, and make to 100 ml. To a 20-ml. aliquot add NaOH to pH 10 (yellow to bromcresol green). To another aliquot add 1*N* NaOH to pH 5.6 (pale blue color), then 2 ml. of 0.1*N* NaOH and 10 ml. of B. Then add 5 ml. of a 5% solution of KCN (to complex any Fe present), 1 ml. of triethanolamine, and 0.2–0.3 g. Eriochrome Black (1 part in 100 NaCl). Titrate with A from red to a pure blue color to determine Ca plus Mg. Another aliquot is brought to pH 5.6, 25 ml. of C are added, the solution is boiled 5 min., and precipitated Ca oxalate is filtered. The filtrate is brought to pH 10; KCN solution, B, and Eriochrome Black are added; and titration is performed as above, yielding Mg. Ca is obtained by difference. Ash of chrome, or chrome-vegetable, leather is dissolved as above, $Cr(OH)_3$ precipitated with NH_4OH, and the determinations carried out as above. In 6 determinations, 1.66 to 1.97% of Epsom salt, and 0.02–0.06% CaO were found. L.M.

Simultaneous Colorimetric Determination of Aluminum and Chromium in Leather. F. Langmaier, D. Kokes, and D. Slovakova. *Kozarstvi*, **8**, 166–68, 198–99 (1958).—Al is determined with Aluminon, and Cr with diphenylcarbazide, using a Pulffrich photometer (Zeiss) or a Spekker photocolorimeter (Hilger). The maximum extinctions are at 5320–80 A. for Al and at 5280–5380 A. for Cr. The colored resin formed by Al with Aluminon is stabilized by gelatin. Al is determined at pH 5.3–5.4; and Cr, in strongly acid solution. Dissolve 0.5 g. leather in 5 ml. $HClO_4$ and 5 ml. of 8*N* HNO_3, in a 100-ml. Kjeldahl flask. Let stand 15 min., then boil for 150–80 min., cool with 20 ml. water, and dilute to exactly 100 ml. Pipet 1 to 5 ml. into a 50-ml. flask, and add 3 ml. of an acetate buffer (470 ml. NH_4OH, 430 ml. of glacial acetic acid, diluted 1:20 with water and titrated to pH 5.3–5.4), and 5 ml. a solution of Aluminon (1 g. in 100 ml. of 1% gelatin solution). Dilute to 50 ml., and heat 10–15 min. at 80°–90°C. to stabilize the color. Cool and measure the color. To determine Cr, mix 1–5 ml. of leather solution with 10 ml. of 10% HCl and 5 ml. of a 1% solution of diphenylcarbazide in acetone. Dilute to 50 ml., let stand 10 min., and measure the color. Obtain the concentrations of Al and Cr from calibration curves. The results by these methods are identical with those from the much slower gravimetric methods. L.M.

Polypeptide Chains in Collagen. V. Kubelka. *Kozarstvi*, **8**, 163–65, 195–97 (1958).—A collagen protofibril is composed of several polypeptide chains which may or may not be identical. Protofibrils from different animals probably contain different polypeptide chains. The results of Deasy (*JALCA*, **51**, 584 [1956]), who found glycine and alanine as end groups in collagen, are regarded as inconclusive. The sequence of amino acids, or groups of amino acid residues, is also uncertain. The work of Grassmann is a first step in elucidating this order. It has been suggested that the polypeptide chains probably contain tripeptides made up of glycine, proline or hydroxyproline, and another amino acid. In 12 amino acids there is one free NH_2 and one free COOH group. The stiochiometric relation of histidine:lysine:arginine is 1:7:10, representing 18 amino acids. The polypeptide chain, therefore, may be composed of 12 × 18, or 216 amino acids. If one amino acid residue has a length of 2.95 A., the polypeptide chain would be 636 A. long, which agrees

well with the electron microscope macroperiod of 640 A. However, proline and hydroxyproline form only 2/9, and not 1/3, of the polypeptide chain, and therefore the above hypothesis may be valid for only the greater part of the chain. Enzymatic hydrolysis does not confirm this simple sequence of amino acids. Certain parts of the polypeptide may be formed by glycide chains, which may be very important for the collagen structure. The basic amino acids probably are concentrated in certain parts of the chain and are absent from other parts. L.M.

Side Chains and Cross Links in the Collagen Molecule. V. Kubelka. *Kozarstvi*, **8**, 232–36, 259–60, 294–97 (1958).—The side chains of collagen, silk, and wool are compared. Stubbings found that they constitute 37.9, 19.4, and 44.5% of the respective molecular weights. Types of side chains are described. Side chains may be coordinative (e.g., H-bonds, length 4.5 A.), covalent (ester bridges length 5–9 A.), or electrovalent (salt bridges, length 10–16 A.). The relation of H-bonds to the theory of tanning is discussed. Glycides may be incorporated into the collagen molecule by ester bridges; acidic polysaccharides containing N and S, e.g., chondroitin sulfuric acid, may be present. Collagen contains about 1% of glycides. Ester bridges are absent in protocollagen and procollagen, and splitting them into lower molecular weight fragments of 20–25 amino acids is therefore relatively easy. Electrovalent linkages are elastic, and are separated by swelling. The influence of acids on shrinkage temperature (T_s) is discussed. Formamide lowers T_s to 15°C. The spiral structure of the collagen molecule is described. Mikhailov considers that collagen is composed of 2 proteins, collastromine (80%) which gives no cross bands in the electron microscope and which is obtained by extracting collagen with a citrate buffer, and procollagen (20%) which is responsible for the cross bands. The latter are caused by glycides present in procollagen. L.M.

Influence of Prolonged Tension on Belting Leather G. Toth. *Kozarstvi*, **8**, 298–301, 336 (1958).—Fatigue of leather has long been known, but no method for measuring it has hitherto been available. Belting leathers with 20, 8, and 2% fat tore, as expected, at elongations of 45, 30, and 20% respectively. When the samples were connected and tested at the same time, they tore in the order of increasing fat content. An apparatus was constructed whereby a leather sample was attached to the short arm of a lever, and weights were attached to the longer arm to give stresses amounting to 80% of the initial tear resistance. The time at which the leather tore was rcorded. As a limit, 32% of the initial load was enough to tear the leather in 271 days. The log of tearing time is a linear function of load, so that the expected life with a given load can be obtained by extrapolation. A belt with initial tearing strength of 3 kg. per sq. mm. was used on a tanning drum. With loads of 2.4, 2.15, and 1.9 kg. it broke after 40, 400, and 2400 min. respectively. By extrapolation it was found that the belt, loaded with 0.65 kg. per sq. mm., should break after 0.8 yr.; actually a belt thus loaded broke after 0.75 yr. Poor-quality belting leather, not tanned through and stuffed with molten fat, had a tear resistance of 2.2 kg. per sq. mm. but a tearing time only 1/100 that of normal leather. The slopes of the curves of log tearing time against load for leathers of initial tearing strengths of 4 and over, 3–4, 2.5–3, and 2–2.5 kg. per sq. mm. are 45, 35, 28, and 20 respectively. The elongations at

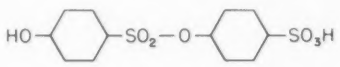
break of individual collagen fibers are different, and during prolonged loading of belting leather the fibers with the smallest elongations break first. Electron microscope pictures show that collagen protofibrils run in different directions. Isolated collagen fibers have tear resistance of 50–60 kg. per sq. mm. Because of the different directions of the fibers, the tear resistance of belting leather is only 1/20 of this value. L.M.

Changes of Epidermis of Rabbits after a Surface Application of Thiophene and Its Mixtures with Purified Toluene. M. Zeman, M. Klatil, and B. Musil. *Kozarstvi*, **8**, 302–3, 309 (1958).—Workers in shoe cement factories using technical toluene as solvent suffer from facial eczema. By experiments with rabbits it is shown that inflammation of the epidermis can be caused by thiophene present in technical toluene to the extent of 40–100 mg. per 100 ml. L.M.

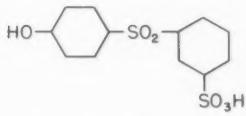
Oxidized Paraffin and Its Use in Tanneries. V. Pilc. *Kozarstvi*, **8**, 325–26 (1958).—Oxidation of paraffin by the usual process with $KMnO_4$ as catalyst produces fatty acids that are unsuitable for use in the leather industry because they cannot be sulfated. A new system of oxidation was worked out. To 300 kg. paraffin (m.p. 50°–52°C.) from naphtha, heated to 120°C., are added 1.5 kg. of fatty acids previously produced and 0.75 kg. $Na_2C_2O_4$. The mixture is blown with 50 l. air per hr. per kg. paraffin, in a double-walled tower heated by thermosiphon circulation of chloronaphthalene. The mixture is heated to 170°–80°C. in 8 hr., held at that temperature for 3 hr., then at 140°–50°C. for 27 hr. Water and volatile oily products escaping from the reactor are absorbed. The water fraction contains lower molecular weight fatty acids. The product (90% of the initial paraffin) contains 50% fatty acids, 10% hydroxy acids, and 26% unsaponifiable matter; acid no. 125.8, saponification no. 237, hydroxyl no. 49, I_2 no. 5, m.p. 31°C. The product is pale yellow. Sulfation is done with 30 kg. H_2SO_4 per 100 kg. product, added over 3 hr. at 40°C., and the temperature is held at 40°C. for 3 hr. longer. The mixture is washed with 78 kg. water and 52 kg. Glauber's salt, added at 32°C. The temperature is raised to 40°C. and held there for 16 hr. The product is neutralized with 12–14 kg. NH_4OH, and is called Sulfopar H. By adding 10% mineral oil, Sulfopar T is obtained. Sulfopar R is made by sulfating a mixture of 80% paraffin oxidation products with 20% rapeseed oil, and blending the resulting product with 10% mineral oil. Sulfopar H, T, and R contain respectively 23.5, 29.6, and 25.5% unsaponifiables, 45.3, 39.7 and 49.5% fatty acids, pH 7.25, 6.95 and 7.20. 10% emulsions are stable for 2 hr. Calf leather fatliquored with 2.7–3.0% Sulfopar H and 0.15% Marseilles soap or Syntapon CP or L (anionic detergents) are fuller, and free from spue, but are drier and a little harder than normal leather. Side upper leather fatliquored with 6% Sulfopar H and 0.3% Syntapon CP was also harder. Sulfopar T gave somewhat softer leather, but best results were obtained with Sulfopar R. Calfskins fatliquored with 3% Sulfopar R and 0.3% Syntapon CP were equal to normal leather, and side leather fatliquored with 6% Sulfopar R and 0.4% Syntapon CP was better—it was soft and had a tight, fine grain. A slight odor of fatty acids was noted at smooth plating, but not in the shoe factory. Wear tests with shoes were successful, and the hygienic properties of the leather were normal. Paraffin oxidation products have also been used for waterproof Cr-retan upper, bag, case, and other leathers. L.M.

Oxidized Paraffin and Its Use in Tanneries. V. Pilc. *Veda a Vyzcum v Prumyslu Kozedelnem*, **4**, 49–64 (1958); cf. preceding abstract.—Paraffins containing the minimum amounts of branched chain and cyclic hydrocarbons are the best raw materials. Paraffins containing 18 to 30 C atoms are preferred; they give fatty acids of 10 to 20 C atoms. Useful sources are: *Gatsch* from the Fischer-Tropsch synthesis, containing 60–70% of straight chain and 30–40% branched chain compounds, no S, and a small amount of olefines, melting at 35°–40°C.; TTH paraffin from hydrogenation of soft-coal tars, extraction with propane and distillation, containing 85–90% normal paraffins, melting at 50°C.; and refined paraffin from naphtha or soft coal. Diagrams of the oxidizing and sulfating apparatuses are given. The products (Sulfopars) are not suitable for fatliquoring white leather. L.M.

Research on the Preparation and Application of a Syntan-Biltan. F. Hejcl. *Kozarstvi*, **8**, 372–75 (1958).—Previous Czech syntans for white leather (Kortamol NNO, etc.,) were inferior to the Swiss Irgatan LV and especially Irgatan RBL. A good syntan for white tannage has been produced by condensing 2 moles of *p*-phenol sulfonic acid, through the $-SO_3H$ group, to form a sulfodepsidic product,



and a sulfone,



These in turn have been condensed with urea and HCHO in the presence of phthalic anhydride to form Biltan. This mixture of complicated, ill-defined substances has, however, interesting properties, as have the products from tricresol instead of phenol. The bleaching effect of Biltan and the stability of the resulting leather to light have been compared with Irgatan RLB and found to be superior. The whiteness was tested on a Zeiss Leucometer, using a MgO plate (whiteness 97.5) as standard. The leathers were exposed 24 hr. to ultraviolet and 150 hr. to sunlight. The whiteness of Cr-tanned calf leathers bleached with Biltan and Irgatan were 67.30 and 66.02 respectively before exposure; after exposure, 65.68 and 64.36. Corresponding values for goat leather were 68.25 and 64.26 before exposure, and 66.48 and 63.91 after exposure. Other syntans (Kortamol NNO, Basyntan FC) gave considerably lower results. Irgatan RBL is believed to be a sulfone with a high content of Al salts. A scheme for the pilot-plant production of Biltan is given. It is clean and colorless, contains 34% solids, no insolubles, 37% tannin (determined at 4 g. tannin per l.), pH of analytical solution 3.8, density 1.29. It is suitable for the complete tannage of reptile and other skins, and has the proper astringency to avoid drawing of the grain. Influence of pH, time, and temperature on bleaching Cr leather with Biltan was studied. The best bleaching of goat leather was obtained with 5–7% Biltan in 250–300% float, at 35°–45°C. for

45–60 min. Loosening of the grain occurs after 120 min. Bleaching is more effective if done before neutralization, but leathers neutralized with 2–4% of $Na_2S_2O_3$ are softer and have a fuller feel. Biltan is especially suited for reptile leather and for making pastel shades of suede from calf, goat and pig skins. It gives more level dyeings than other syntans; the best application is at 40°–50°C. at pH 3.15–4.4. Pilot-plant results have been confirmed by large-scale tests. L.M.

Chemical Analysis of Chrome-Vegetable-tanned Leathers. A. Blazej. *Kozarstvi*, **8**, 227–31, 239 (1958).—A review and criticism of Czech standards. Samples should be cut to cubes passing a 3 x 3 mm. sieve and retained by 2 x 2 mm. Errors in determining water are pointed out; the only exact method is said to be the determination of dielectric constant. Ash should be determined in the original leather and after water extraction, and percentage of Cr_2O_3 should be subtracted. The Cr_2O_3 content of vegetable-tanned leather is lower than the amount originally bound, as considerable displacement occurs during retannage. Part of the Cr is water-soluble and should not be included with "Cr tanning substance". Extraction by CCl_4 gives a higher fat percentage than petroleum ether. Determination of water solubles at 45°C. is recommended; extraction at 25°C. is rejected as representing "purely commercial interests." The method is wholly empirical and depends greatly on degree of subdivision. Leather samples cut to 3 x 3 mm. cubes gave 17.1% water solubles, while 6 to 7 mm. cubes gave only 12.8%. The original Kjeldahl nitrogen determination in Cr-vegetable leather is difficult, the digestion requiring 3 to 4 hr. The best catalyst is a mixture of 100 g. K_2SO_4 with 5 g. $CuSO_4 \cdot 5H_2O$ and 5 g. Se. With this mixture, digestion of a 0.5-g. sample in 20 ml. H_2SO_4 takes only 40 min. Determination of N in leathers in which tannin was fixed by N-containing compounds, such as methylol urea, cannot serve for calculating hide substance. Calculation of hide substance from a colorimetric determination of hydroxyproline, as recommended by Lollar, is to be preferred. If the nitrogen determination is done after water extraction, soluble ammonium salts do not interfere, except some NH_4 salts of syntans. The pH of the water-soluble extract depends on the particular vegetable retannage and generally is lowered on aging of the Cr complex. **II. The Calculation of Characteristic Constants**. *Ibid.*, 291–93, 335.—Tanning value, yield value, and "leather substance" are characteristic indexes long used in the analysis of vegetable leather, but in Cr-vegetable leather the relation of fixed tannin to "Cr tanning substance" is more important than their sum. Cr tanning substance is about 2 to 4 times the Cr_2O_3 content. Cr tanning substance may be taken as the sum of $Cr_2O_3 + SO_4$ after extraction of water solubles. If masked Cr liquors are used, the other anions fixed along with Cr must also be determined. For calculating tanning value, it is proposed that fixed tannin and Cr tanning substance should be calculated separately, because an over-all tanning value is not a characteristic of Cr-vegetable leather. If the same method of calculation used for vegetable leather is employed, then Cr_2O_3 should be deducted from the ash. Another way is to calculate the sum of Cr_2O_3 and fixed tannin, and to state the ratio of Cr_2O_3 to tannin. Calculation of yield value presents no difficulties, but calculation of volume yield, recommended by Bergmann, is more important. Apparent specific gravity should be determined after a thorough wetting and drying to eliminate the effect of rolling

in the case of sole leather. **III.** *Ibid.*, 376–78.—Calculation of analyses to a 14% water basis is criticized. Only the ratio of Cr_2O_3 to hide substance gives a clear idea of the intensity of Cr tannage and is not affected by variations in fat content, etc. Permitted limits of Cr_2O_3 content should be stated in the standard. All other components should be calculated on the hide substance basis. L.M.

The Production of Suede Leather. H. Wicki. *Kozarstvi*, **8**, 215–16 (1958).—Suede leather retanned with vegetable tannins or dicyandiamide resins cannot be dyed successfully in deep shades. Retannage with Cr, Cr-Al, or perhaps Cr-Zr is advised. Unpickled pelt, at pH 6.5, is tanned for 45–60 min. in 70% float containing $KCr(SO_4)_2$ equal to 2% Cr_2O_3 on the pelt weight. The slightly swollen skins are transferred to a second bath containing 2% Cr_2O_3, 42–50% basic, in 70% float and 0.3–0.5% of a cationic detergent or a mixture of the latter with sperm oil. The bath is nearly exhausted in 2 hr. Then water is added to make 150% float, and the skins swell slightly. A full leather that can be dyed easily is obtained. The sooner the cationic detergent is given, the better the results. Quarternary ammonium salts, containing the minimum of fatty components, are suitable cationic detergents. Cationic fatliquors are preferred, as the resulting leather can easily be buffed. If skins for suede leather are sorted out after Cr tannage, a Cr-Al retannage with addition of the cationic detergent is necessary. A suede with a nap that holds finger marks is obtained by a full fatliquor before the first drying. Cr soaps formed on the surface of the fibers give them the required sheen. Leathers fatliquored partly before and partly after drying are less brilliant. Anion-active wax emulsions stable at pH values over 7.5 give good results. The dyeing of suede may be compared to column chromatography of the dyes employed. To obtain pastel shades one must have a pH of 6.5 throughout the whole thickness of the leather. Striking through depends on the volume of liquor used; a dye which strikes through in 800% liquor dyes only the surface in 1200% liquor. The preferred system for getting deep shades is to dye first with 3–4% dye in 200% liquor (on the dry leather weight). Practically all the liquor is absorbed, and the color is struck through. Then 8% dye in 2000% liquor is added, and the additional dye is fixed in about 1/6 of the leather thickness, which is advantageous for buffing. A 10 to 20% better utilization of dye is the result. Neolan dyes are solubilized by sulfonation, and Cibalan dyes, containing 2 Cr atoms per molecule, by addition of sulfonamides; they are, in reality, highly dispersed organic pigments. Cibalan dyes give deeper shades than Neolan but present difficulties with respect to striking through. Spraying pigments on suede is not a suitable method of evening up the color; it is better to pair the skins flesh to flesh and stake lightly. Black suede, however, can be sprayed with aniline black pigments containing a very little binder. In the discussion it was stated that retannage with Cr alum can be replaced by a 1:2 mixture of Cr and Al alums, with improved intensity and light stability of the color. L.M.

Progress in Shoe Cements. G. Rojcik. *Kozarstvi*, **8**, 176–79 (1958).—The adhesion of a shoe cement should equal its cohesion. For cementing plasticized polyvinyl chloride (PVC) a cement composed of Vinol H (a copolymer of vinyl chloride and vinyl acetate) may be used; it gives a tear strength of 3.5 kg. per sq. cm., and the excess cement peels off the PVC.

A nitrile rubber cement gives the same tear strength, but the cement remains on the PVC surface because its cohesion is lower than its adhesion. A cement containing 2 Vinol H and 3 nitrile rubber has a tear strength of 6.5 kg. per sq. cm. Chloroprene cements are best if they contain both crystalline Neoprene AC and amorphous Neoprene WH. An idea as to the crystalline and amorphous components can be obtained from X-ray diagrams and measurement of hardness after plasticization. Polychloroprenes are now the most important raw materials for cements. Thermoplastic cement is used in the molten state: thermoactive cement is applied to the surfaces to be bonded, dried, and then activated by heating, preferably by infrared rays. Cements from dissolved polychloroprenes are most important. They soften at 60°C., but this can be raised to 80°C. by adding phenol-HCHO resins. A basic solution of Neoprene containing 2% sulfur is stable for 6 months, but it gelatinizes within 24 hr. if 20% PbO is added. A solution with 2-butyl aldehyde in butyl amine gelatinizes in 18 hr., and a mixture of the two in 3 hr. Thermal stability of shoe cements is raised effectively by cross-linking the linear molecules of polychloroprenes by tri-isocyanates (Desmodur R and TH). Dichloroethane is the best solvent, but it is very toxic. Nitrile rubber cement is best for plasticized PVC. Special cements made from polyurethanes (Desmocolls) can be used universally but are too expensive compared to polychloroprene cement. Various cements from the U.S., Canada, Great Britain, Germany, and the USSR are described. L.M.

Czechoslovak Syntans from Dihydroxy Phenols. H. Weber. *Kozarstvi*, **8**, 238–39 (1958).—The composition of the phenosolvan extract of Bohemian coal carbonization products is given. This extract can be fractionated into 40% of a phenol-cresol fraction, 45% of a pyrocatechol fraction, and 5% of an intermediate fraction. The pyrocatechol fraction is called Difen. A better-refined fraction, called Optol, contains 7% distilling below 248°C. and 93% distilling to 268°C., and is composed of 75% pyrocatechol, 2.2% homopyrocatechol, 1.7% isohomopyrocatechol, i.e., 4,5-dimethylpyrocatechol, 0.9% of higher homologs of pyrocatechol, and 0.5% neutral oils. Syntans have been made by condensing Difen or Optol with 2-naphthol-6-sulfonic acid, containing a considerable amount of phenolic OH groups. Kortan Qu is made by condensing 1 mole of 2-naphthol-6-sulfonic acid with one pyrocatechol; it corresponds to USSR Syntan No. 4. Another syntan (Kortan QD) made from one mole of 2-naphthol-6-sulfonic acid and 2.35 moles pyrocatechol has even better properties. Syntans containing more than 80% of dihydroxy phenols are very astringent, and their purity exceeds 90. Syntans from 1 mole of 2-naphthol-6-sulfonic acid and 4 moles pyrocatechol have been made in the laboratory; they tan even better but have no dispersing action on vegetable tannins. Leathers tanned with these syntans darken in sunlight but may be made lightfast by adding 1% pyrosulfite on the weight of the syntan. L.M.

PATENTS

***Iso*thiouronium Salts; Finishing Leather.** Brit. Pat. 815,226. Farbwerke Hoechst Aktiengesellschaft Vorm. Meister, Lucius & Bruning. Appl. July 29, 1955.—Skins, pelts and leather are treated with emulsions comprising chlorinated hydrocarbons and *iso*thiouronium salts containing a tri-halogeno-alkyl group or a dihalogeno-alkenyl group and prepared by reacting tetrahalogeno-alkane of the formula

$$(\text{halogen})_3C—(CH_2—CH_2)_n\text{-halogen}$$

or a trihalogeno-alkene of the formula

$$(\text{halogen})_2C{=}CH—CH_2(CH_2—CH_2)_{n-1}\text{-halogen}$$

(wherein the halogen is chlorine or bromine and n is an integer from 1 to 10) with thiourea or a substituted thiourea, e.g. N-alkyl-, N:N^1-di-alkyl- or N:N-dialkyl-thioureas wherein the alkyl groups may be wholly or partially replaced by aryl groups, or N:N-alkylene-thioureas. In an example retanned bark-tanned bottom leather is treated, in the vat following the retanning, with a mixture of chlorinated kogasine (95 parts by weight) and a trichloroalkyl-*iso*-thiouronium chloride having an average chain length of 13 carbon atoms (5 parts by weight), thereby fixing the tanning agent and allowing the leather to dry out clear and uniformly.

Impregnating Leather with Polyurethanes. Brit. Pat. 815,185. Imperial Chemical Industries Ltd. Appl. March 10, 1958.—Leather is impregnated with polyesters or polyesteramides in the presence of polyfunctional isocyanates. Preferably the leather is deaerated by a vacuum treatment before impregnation and the polyester or polyesteramide modified by reacting from 0.75 to 3.0 mols. of polyfunctional isocyanate with each mol. of polyester or polyesteramide. The leather may be soaked in polyester or polyesteramide and then in a dilute solution of the isocyanate in an inert solvent, or the polymer and the isocyanate may be mixed before treating the leather. The polyesters or polyesteramides may be made by interaction of glycols, such as ethylene glycol, 1:2-propylene glycol, 1:3-propylene glycol, diethylene glycol, triethylene glycol, tetramethylene glycol, hexamethylene glycol and decamethylene glycol, with dicarboxylic acids, such as succinic, glutaric, adipic, suberic, azelaic, sebacic, phthalic, isophthalic and terephthalic acids, plus, if desired, proportions of amino and/or polyhydroxy compounds, such as monoethanolamine and pentaerythritol. Specified isocyanates are p:p^1-diisocyanato-diphenylmethane, toluylene diisocyanate, hexamethylene diisocyanate, diphenylmethane diisocyanate. Specified solvents are acetone, ethyl acetate, nitropropane, methylene dichloride, ethylene dichloride, methylethyl ketone.

Method of Preparing Gelatin or Glue. U. S. Pat. 2,908,615. H. L. Keil, Claredon Hills, Ill., assignor to Armour and Company, Chicago, Ill., a corporation of Illinois. Appl. February 24, 1956.—1. The method of extracting a material selected from the group consisting of gelatin and glue from pork skins which comprises treating the skins with a sterilizing agent, subjecting the sterilized skins to the action of added living yeast-type organisms to condition said skins, and then extracting a material selected from the group consisting of gelatin and glue from the conditioned skins with water.

Amine Modified Acetals. U. S. Pat. 2,890,242. B. H. Kress, Lafayette Hill, Pa., assignor to Quaker Chemical Products Corporation, Conshohocken, Pa. a corporation of Pennsylvania. Appl. September 14, 1955.—1. A polymeric acetal condensation product comprising the reaction product made under acidic conditions and at reflux temperatures of a salt of an amino alcohol containing at least two hydroxy groups and an aldehyde, said salt being selected from the group consisting of amine salts and quaternary ammonium salts of strong

acids and said aldehyde containing not more than eight carbon atoms in monomeric form, said condensation product having at least two aldehyde units and at least two polyhydric alcohol units per molecule. Useful at tanning adjuvants.

Leather Article. U. S. Pat. 2,911,327. C. F. Dudley, Midland, Mich., assignor to Dow Corning Corporation, Midland, Mich., a corporation of Michigan. Appl. August 7, 1956.—2. A leather article suitable for use as a semi-permeable oil seal comprising leather having a surface coating of a cured siloxane consisting essentially of from 5 to 20% by weight of a methylhydrogenpolysiloxane and from 80 to

95% by weight of a dimethylpolysiloxane gum of at least 1,000,000 cs. viscosity at 25°C.

Aftertreatment of Leather Dyeings. U. S. Pat. 2,908,543. J. S. Kirk, East Greenbush, N. Y., assignor to General Aniline & Film Corporation, New York, N. Y., a corporation of Delaware.—Appl. June 29, 1956.—1. A process for improving the fastness to wet treatments of leather dyeings comprising treating such dyeings with an acidic aqueous solution, substantially devoid of copper compounds, of the product of the reaction of about 1 to 3 moles of formaldehyde, 0.5 to 1 mole of an ammonium salt of a strong acid and 1 mole of dicyandiamide in an acidic aqueous solution, said reaction having been carried out at a temperature below about 45°C.

Waterproofing. Brit. Pat. 815,944. Farbenfabriken Bayer A.G. Appl. March 7, 1957.—A waterproofing agent for textiles, e.g. cotton, rayon or nylon, paper or leather, comprises an aqueous paraffin emulsion containing an ester wax and a complex Werner type chromium salt containing one or more acyl groups. The wax emulsions may be added to hot solutions of the chromium complex salts, the *p*H reduced to between 3 and 4, and the mixtures cooled. The chromium complexes may be made by boiling chromium trichloride and sodium stearate or stearoyl-amino salicylic acid under reflux with isopropyl alcohol and then treating with sodium hydroxide under heat. The paraffin emulsion may be made by treating paraffin of melting point 52–54°C., ceresine and bleached montanic acid partially esterified with glycol with potassium carbonate and sodium chloride or with diethylamine oleate and ethanolamine in water and at temperatures above the melting points of the waxes. The wax emulsions may be added to hot solutions of the chromium complex salts, the *p*H reduced to between 3 and 4, a buffering solution of sodium acetate and acetic acid being employed, and the mixtures cooled. Alternatively, the mixture may be neutralized with a solution of hexamethylene tetramine, and urea may be added. Specification 324,631, [*Class 22*], is referred to.

Process for the Production of Dicyandiamide Resins by the Melt Process. U. S. Pat. 2,884,403. B. Zorn, Koln-Deutz, and G. Mauthe, Opladen, Germany, assignors to Farbenfabriken Bayer Aktiengesellschaft, Leverkusen, Germany, a corporation of Germany. Appl. May 24, 1955. Claims priority, appl. Germany May 25, 1954.—1. A process for the production of tanning

agents precipitable by acids which comprises heating and melting, at a temperature between 70° and 200°C., a substantially anhydrous mixture of (1) mixed dicyandiamide and urea, the proportion of the urea being not more than 90% of the weight of the total of dicyandiamide and urea or less than about 1 mol for 1 mol of the dicyandiamide, (2) paraformaldehyde in the proportion of 0.5–8 mols of formaldehyde equivalent for 1 mol total of dicyandiamide and urea, and (3) the sodium salt of the condensation product of about 1 mol of naphthalene sulfonic acid with from 0.66 to 1 mol of formaldehyde, the said condensation product being in proportion to cause the product to be precipitable by an acid, after cooling, to remain completely soluble in water or storage of the aqueous solution.

Permeable Abrasion Resistant Artificial Leather. Brit. Pat. 816,095. Spirit, J., and Smejkal, V. Appl. Sept. 2, 1957.—A permeable and abrasion-resistant artificial leather comprises a flexible base, e.g. a textile material, and a surface layer on the base compound of a set of zones of porous synthetic organic polymer material distributed over the base and interfitting with a complementary set of zones of abrasion-resistant synthetic organic polymer material. The surface layer may be composed of at least one set of zones consisting of a pattern of straight strips of polymer material or the zones of both sets are complementary patterns of irregular shape and together form a mosaic. The abrasion-resistant polymer material, which may be non-permeable, and the porous polymer material may include polyvinyl chloride. The artificial leather may be produced by (i) forming an openwork layer on the flexible base and then filling the cavities of the layer with another synthetic organic polymer material, one material being porous and the other being abrasive-resistant; (ii) forming a continuous layer of porous polymer material on the flexible base, forming design cavities in the layer, and filling the cavities with the abrasion-resistant polymer material; or (iii) forming an openwork layer of zones of abrasion-resistant polymer material spaced to form a design, the cavities between the zones being filled with the porous polymer material. The coating compositions may contain softeners, e.g. dioctyl or dibutyl phthalate, glycerol, fillers and leavening agents which may be soluble in water, lower alcohols and ketones, or may decompose at high temperatures, e.g. sodium and potassium chloride, sodium sulphate, calcium chloride, ammonium carbonate, kaolin, barium sulphate, and calcium stearate.

Process for the Preparation of Coating of Soft Resins from Polyisocyanates and Compounds Containing Hydroxyl Groups. U. S. Pat. 2,897,166. K. Eitel and F. Schmidt, Leverkusen, and G. Mauthe, Opladen, Germany, assignors, by direct and mesne assignments, of one-half to Farbenfabriken Bayer Aktiengesellschaft, Leverkusen, Germany, a corporation of Germany, and one-half to Mobay Chemical Company, Pittsburgh, Pa., a corporation of Delaware. Appl. Nov. 5, 1954. Claims priority, appl. Germany Nov. 6, 1953.—1. A process which comprises applying to a porous surface a solution in an inert organic solvent of a polyisocyanate, a soft polyfunctional resin comprising a polyester prepared from a polybasic carboxylic acid and a substantial excess of a polyhydric alcohol and a metallic soap selected from the group consisting of titanium and zirconium metallic soaps, and subsequently allowing the solution applied to said surface to dry to thereby obtain a high luster, smooth, crater-free coating on leather.

Coating Leather. Brit. Pat. 816,630. Rohm & Haas Co. Appl. Oct. 25, 1956.—In providing leather and the like with a plurality of protective coatings of which the primary coating comprises an aqueous dispersion of a water-insoluble linear polymer formed from monoethylenically unsaturated monomers containing a tertiary amine group while the subsequently applied coatings contain film-forming polymers derived from vinyl, acrylic monomers, cellulose derivatives &c., there is added with the primary coating or as a separate coating between the primary coating and the outer coatings, a water dispersible condensate containing epoxide groups having the structural formulae III, IV, V or VI as specified below.

(III) $CH_2\text{—}CHCH_2O(CH_2CH(OH)CH_2O)_xCH_2CH\text{—}CH_2$ (O bridges)

(IV) $CH_2\text{—}CHCH_2O(CH_2)_yOCH_2CH\text{—}CH_2$ (O bridges)

(V) $CH_2\text{—}CHCH_2O(C_mH_{2m}O)_zCH_2CH\text{—}CH_2$ (O bridges)

(VI) $CH_2\text{—}CHCH_2O(\text{Ø}C(CH_3)_2\text{Ø}O)_pCH_2CH\text{—}CH_2$ (O bridges)

where x is 1–3, y is 2–10, p is 1–3, z is 1–5, m is 2–4 and Ø is the *p*-phenylene group. The polymers having tertiary amine groups are derived from alkyl substituted vinyl pyridines or from compounds of formula

(II) $CH_2{=}C(R)AYNR^1R^{11}$

where R is H or CH_3, A is O, S, —COO— or CONH—, R^1, R, when not directly attached to each other, are phenyl, benzyl, cyclohexyl or alkyl and when directly attached are morpholino, piperidino or pyrrolidino residues. Among the many examples specified of formula (II) are dialkyl amino acrylates, methacrylates, vinyl ethers or sulphides, acrylamides, and morpholino-, piperidino-, or pyrrolidino-alkyl acrylates, methacrylates, vinyl ethers or sulphides. In an example: (a) a copolymer obtained by copolymerizing a mixture of ethyl acrylate, butylacrylate and vinyl pyridine in presence of ammonium persulphate, sodium hydrosulphite and triethanolamine as catalysts is pigmented with a dispersion of red iron oxide in water, sodium lauryl sulphate, *t*-octyl phenoxy-polyethoxyethanol and methyl cellulose, and the pigmented dispersion is used to swab leather upholstery. The dried coating is then further coated with a pigmented dispersion consisting of red iron oxides, a plasticizer obtained by reacting sebacic acid with propylene glycol, and a vinylchloride-vinyl acetate copolymer in a solvent mixture comprising ethoxyethyl acetate, methyl ethyl ketone, and aromatic, naphthenic and aliphatic hydrocarbons, the pigment dispersion also containing an epoxy compound of formula III above, (c) the leather is then given a final coating by spraying it with a vinyl chloride-vinyl acetate copolymer in a solvent mixture comprising ethyoxyethyl acetate, methyl ethyl ketone and xylene.

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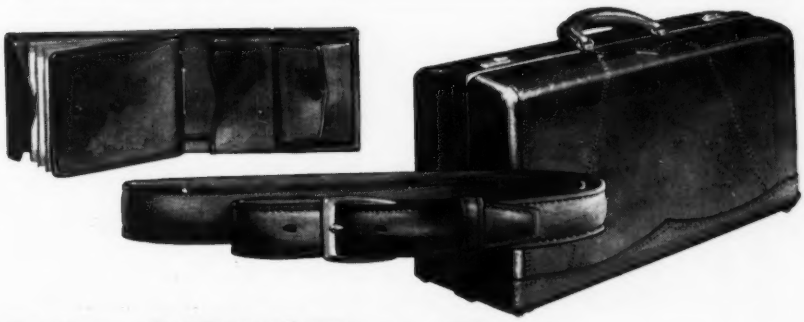

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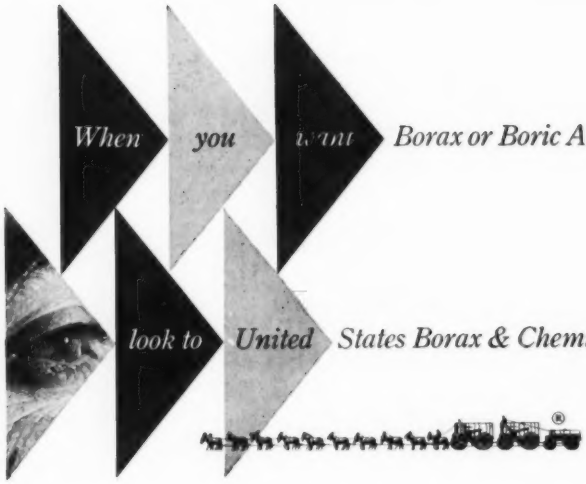

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born of Science is
a chemical Process
Industry — Be Prepared

Fred O'Flaherty

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OKLAHOMA!

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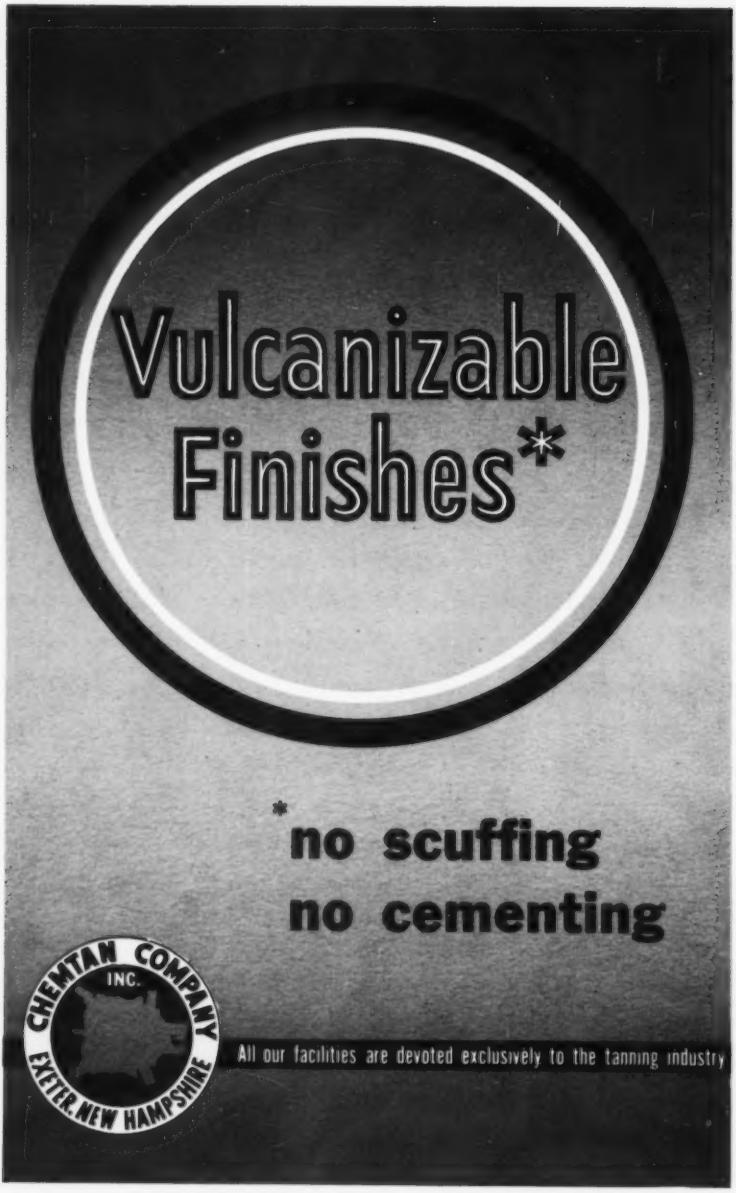
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